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Truck Washing Terminal Water Pollution Control

Matlack, Inc.
Lansdowne, PA

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June 1980

TRUCK WASHING TERMINAL WATER POLLUTION CONTROL

by

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Grant No. S803656-01

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16. ABSTRACT

A laboratory and pilot-scale investigation of a treatment sequence, including physical, chemical, and biological treatment steps led to a full-scale installation for the treatment of tank truck washing wastewater. The system included gravity separation equalization, neutralization, dissolved air flotation, mixed-media filtration, carbon adsorption, and biological treatment. This facility treated 15,000 gallons per day (6.6×10^{-4} m^3/s) of wastewater from the Matlack, Swedesboro, New Jersey, truck washing terminal for proposed subsequent discharge to a tributary of the Delaware River. Following pre-treatment for the removal of suspended solids and insoluble oils and greases, carbon adsorption was used for detoxifying the wastewater prior to biological stabilization. The total system demonstrated an overall treatment effectiveness averaging greater than 90% removal of COD and 99% removal of oils and greases and phenolic compounds. The cost of treatment was $48.92 per 1,000 gallons (3.78 m^3) of wastewater treated. This equated to a unit cost of $24.46 per trailer cleaned. A toxic substance study indicated that organic compounds were eliminated through the treatment train.

A further pilot plant investigation was made to determine if chemical oxidation through the use of ozone and/or ozone/UV could be substituted for activated carbon to reduce COD and transform toxic organics to a biodegradable form.

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FOREWORD

When energy and material resources are extracted, processed, converted, and used, the related pollutional impacts on our environment and even on our health often require that new and increasingly more efficient pollution control methods be used. The Industrial Environmental Research Laboratory - Cincinnati (IERL-Ci) assists in developing and demonstrating new and improved methodologies that will meet these needs both efficiently and economically.

This report "Truck Washing Terminal Water Pollution Control", documents the full-scale evaluation of a 15,000 gallon per day (6.6×10^{-4} m^3/s) physical - chemical - biological system for treatment of wastewaters generated from the cleaning of tank truck interiors. The prevailing treatment practices in the tank truck industry have generally been limited to sedimentation, neutralization, evaporation ponds and lagoons. The "Draft Development Document for Proposed Effluent Guidelines for the Trucking Segment of the Transportation Industry" released in April, 1974, recommended the use of treatment techniques which were available but not demonstrated specifically for the tank truck industry. The effectiveness and economics of these techniques have now been demonstrated by the EPA. This treatment system may also have application to the drum, railroad tank car, barge and other bulk chemical distribution industries which must clean their equipment between shipments. For further information on the subject, contact the Industrial Pollution Control Division of the Industrial Environmental Research Laboratory - Cincinnati, Ohio 45268.

David G. Stephan
Director
Industrial Environmental Research Laboratory
Cincinnati

ABSTRACT

A laboratory and pilot-scale investigation of a treatment sequence, including physical, chemical, and biological treatment steps led to a full-scale installation for the treatment of tank truck washing wastewater.

The system included gravity separation, equalization, neutralization, dissolved air flotation, mixed-media filtration, carbon adsorption, and biological treatment. This facility treated 15,000 gallons per day (6.6×10^{-4} m^3/s) of wastewater from the Matlack, Swedesboro, New Jersey truck washing terminal for proposed subsequent discharge to a tributary of the Delaware River.

Following pre-treatment for the removal of suspended solids and insoluble oils and greases, carbon adsorption was used for detoxifying the wastewater prior to biological stabilization.

The total system demonstrated an overall treatment effectiveness averaging greater than 90% removal of COD and 99% removal of oils and greases and phenolic compounds.

The cost of treatment was $48.92 per 1,000 gallons (3.78 m^3) of wastewater treated. This equated to a unit cost of $24.46 per trailer cleaned.

This report is submitted in fulfillment of EPA Grant Number S803656-01 under the partial sponsorship of the Environmental Protection Agency. It covers a period of operations from February, 1976 to June, 1977.

A toxic substance study was also conducted. This was somewhat inconclusive since the reference compounds could not be identified after the initial treatment step. However, indications were that organic compounds were eliminated through the treatment train.

A further pilot plant investigation was made to determine if chemical oxidation through the use of ozone and/or ozone/UV could be substituted for activated carbon to reduce COD and transform toxic organics to a biodegradable form.

This latter pilot study was also accomplished under EPA Grant Number S803656-01 and covers a time period from September, 1977, to January, 1979.

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ABBREVIATIONS AND SYMBOLS

cm	---	centimeter
cm^2	---	square centimeter
kg	---	kilogram
kg/m^2	---	kilogram per square meter
kPa	---	kilopascal (kN/m^2)
l	---	metric liter
m	---	meter
m^2	---	square meter
m^3	---	cubic meter
m^3/s	---	cubic meters per second
mg/l	---	milligram per liter
ppb	---	parts per billion
ppm	---	parts per million
psi	---	pounds per square inch
sf	---	square foot
~	---	approximately
DAF	---	Dissolved air flotation
RBF	---	Rotating biological filter
API	---	American Petroleum Institute
BOD	---	Biochemical oxygen demand
COD	---	Chemical oxygen demand
pH	---	Defined as the negative logarithm of the hydrogen ion concentration indicating the degree of acidity or alkalinity
O & G	---	Oil and grease
JTU	---	Jackson turbidity units
SS	---	Suspended solids
GC	---	Gas chromatography
MS	---	Mass spectrophotometer
NPDES	---	National Pollution Discharge Elimination System
New Jersey DEP		Department of Environmental Protection

ACKNOWLEDGEMENTS

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The Ozone/UV Chemical Oxidation Study was contracted to General Electric, Re-Entry and Environmental Systems Division. Dr. K. K. Jain was the Project Engineer and J. H. Lazur performed the actual experiments.

Mr. Robert Keller of Matlack's Swedesboro Terminal was the plant operator. Without his diligent effort, this project could not have been successful.

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The support and guidance of Mr. Ron Turner and Mr. Mark Stutsman of the EPA-IERL Cincinnati is sincerely appreciated.

SECTION 1

INTRODUCTION

Matlack, Inc. is one of the largest for-hire bulk motor carriers in the nation. Founded in 1888 as a hauler of construction materials, the Company converted during the early 1930's to hauling petroleum products in tank vehicles. As chemical and petrochemical production grew, the tank truck transporters developed vehicles and know-how to handle a wide variety of products in bulk quantities. Today, Matlack operates about 2,000 tractors (power units) and 3,800 specialized tank semi-trailers.

Tank truck carriers operate more than 90,000 trucks in the U.S. About one-third of these are operated by major petroleum and chemical companies. These fleets haul products of the parent company and are generally dedicated to specific products. Since these vessels remain in the same service, it is generally not necessary to clean the interiors between loads.

The remaining 60,000 or so tankers constitute the industry common carrier fleet and are "for public hire". Some of these tankers are also "dedicated" to carry specific products and don't require frequent interior cleaning. However, a great many are in general service which necessitates cleaning between product changes. Matlack has 56 terminal locations. At 28 of these terminals, facilities are provided to clean the interiors of the tank trailers. During 1976, over 100,000 trailers were cleaned internally at Matlack facilities.

The majority of the tank interiors are cleaned by means of a hot caustic solution recirculated through a omni-directional spinning spray nozzle inserted into the tank manhole. This is followed by a fresh hot water rinse through the same device but with the rinse water directed to the floor drain. It is this rinse water that is the primary source of the wastewater problem addressed here. This wastewater is a highly alkaline emulsion containing suspended and dissolved solids, plus soluble organics, and hydrocarbons in a colloidal or emulsified state.

Since 1966, Matlack had been investigating various pre-treatment systems for sewer discharge. These included chemical flocculation followed by vacuum filtration, ultrafiltration, screening and conventional biological treatment and gravity separation followed by dissolved air flotation. Gravity separation, equalization and dissolved air flotation appeared the best and Matlack installed the first system at its Lester, Pennsylvania terminal in 1974. This was found to produce a treated

effluent that, while high in BOD and COD, was acceptable to the Tinicum Township Sewage Treatment Plant. A surcharge was made for the excess BOD and suspended solids.

With the success of the treatment at its Lester terminal and, realizing that further treatment might be required at some of its washing facilities, Matlack instituted a pilot study at the Lester terminal aimed at evaluating secondary treatment of the dissolved air flotation effluent.

This pilot study consisted of running a slip stream of the dissolved air flotation unit effluent at 2 gpm (1.0×10^{-4} m^3/s) through a mixed-media filter and then through a packed bed of granular activated carbon. Biodegradability tests were then run on both the filter and carbon effluents. While the filter effluent demonstrated a consistent resistance to biological treatment, the activated carbon pilot system was effective in reducing the toxic nature of the wastewater, thus rendering it amenable to biological treatment.

Adsorption isotherms and dynamic column studies conducted at an activated carbon supplier's laboratories confirmed this information.

Matlack's terminal at Swedesboro, New Jersey is a typical operation hauling a wide variety of chemical and petroleum and other products. (See Table 1). To maximize the opportunity for two-way hauls, many trailers are cleaned at this terminal where the load originated in other parts of the country. Representative products cleaned are oils, detergents, sugars, phenols, latex, resins, plasticizers, paints, and a spectrum of non-chlorinated and chlorinated aliphatic and aromatic solvents.

An average of 780 tankers are cleaned at this terminal monthly resulting in an average daily production of 15,000 gallons (56.78 m^3) of wastewater. This works out to an average of 500 gallons (1.89 m^3) per vessel. However, it also includes the wash and rinse water from exterior cleaning of the tractors and trailers, and the cleaning of product pumps and hoses.

The Swedesboro, New Jersey terminal of Matlack is located in a rural, agricultural area. No publicly owned treatment works (POTWs) have collection lines within any reasonable distance, and none are expected to be constructed within the next 5 to 10 years. Therefore, it became necessary for Matlack to develop an advanced wastewater treatment process to enable them to achieve an effluent that would be permitted to be discharged to an adjacent tidal creek that is a tributary of the Delaware River. Permits are required from EPA, New Jersey DEP and the Delaware River Basin Commission.

TABLE 1. PRODUCT MIX OF TANKER CARGO *

Cargo	# Cleaned	Cargo	# Cleaned
Acetone	1	Alcoholic Liquor	1
Catalyst	1	Alkylates	2
Undefined	10	Phenol [1]	7
Gasoline	2	Animal Oils NOI [1]	1
Solvents-Petroleum	23	Calcium Chloride Sol	1
No. 2 Fuel Oil	1	Sodium Nitrite Sol.	14
Lube Oil	225	Sodium Hydrosulfide	2
No. 6 Fuel Oil	1	Latex	114
Plasticizing Oil	1	Resin	91
Toluene	20	Plasticizer	219
Fuel Oil Additive	3	Anhydrous Ammonia	2
Carbon Black Oil	9	Sulfuric Acid	1
Transformer Oil	3	Caustic Soda	19
Water	1	Lard	14
Tar Oil	16	Hydrofluoric Acid	1
Naphthalene	1	Aluminum Chloride	1
Road Paving Compound	10	Styrene	1
Waste	5	Silicate of Soda [1]	1
Dye Intermediate	1	Alcohol NOI [1]	1
Aminoethyl Amine	1	Chemicals NOI	11
Aromatic Bottom Dist.	1	Tallow [1]	1
Divinylbenzene	1	Acid NOI [1]	2
Ammonium Thiosulfate	19	Benzyl Chloride	1
Orthodichlorobenzene	2	Ether NOI [1]	1
Ammonium Thiocyanate	1	Fatty Acid	8
Sodium Sulfide Sol	4	Glue	1
Wax	52	Sugar Syrups	5
Butyl Alcohol	3	Liquid Sugar	8
Sodium Bichromate	1	Ethylene Glycol	2
Carbon Tetrachloride	1	Soap	2

* (Not all inclusive of variety of products cleaned, but representative for a given month at Matlack's Swedesboro washing terminal).

1. "Not otherwise indicated by name" a Bill of Lading description for ICC identification.

SECTION 2

CONCLUSIONS

The results of the full-scale studies evaluating the treatment of tank truck washing wastewater demonstrated the technical feasibility and process economics of the approach employed. The treatment sequence of physical-chemical pre-treatment, carbon adsorption, and biological degradation proved to be effective in the treatment of a highly variable, sometimes toxic wastewater which had previously defied effective means for complete treatment.

Activated carbon appears to be a viable treatment process for tank truck washing wastewater. Despite the high cost, (40-60% of total treatment costs), activated carbon should be considered in the sequence of treatment steps, where surface water discharge standards must be met.

The key to the success of the treatment process was the use of granular activated carbon as a detoxifying step prior to a biological process. The activated carbon served to preferentially remove high molecular weight toxic or refractory organics while passing low molecular weight organics for biological treatment. Thus, the treatment sequence capitalized on the effectiveness of the activated carbon and biological processes combining them in a fashion that resulted in a final effluent capable of meeting contemporary stream standards.

While it appeared demonstrated that the Rotating Biological Filter (RBF), if properly sized, could provide the required biological polishing, the mechanical problems encountered discouraged further development of this design. It was, therefore, decided to investigate a new fluidized bed biological treatment process. Pilot testing of this approach confirmed the feasibility.

Results of the testing indicate potential wide application of the technology employed recognizing transferability to many other mixed waste treatment problems. Some of these areas might include railroad tank car cleaning, drum cleaning and recycling, or the treatment of other mixed chemical wastewaters resulting from off-site waste hauling and treatment operations.

SECTION 3

DESCRIPTION OF UNIT PROCESSES

Wastewater treatment begins at the Swedesboro facility by the segregation for separate disposal of any products and solvent wastes retained in the tank trailer prior to washing. This heel amounting to 1 to 500 gallons (1.89 m^3) is drained from the tankers and drummed for shipment to an approved landfill. This step reduces considerably the concentration of organic materials discharged during the washing process.

The wastewater produced in the subsequent washing operation is an emulsion of oils containing a variety of organic and some inorganic chemicals. It varies in appearance from an off-white to various shades of brown and is generally opaque in nature. The Swedesboro treatment system serves to remove the oils and greases and to reduce the concentrations of organic contaminants to levels suitable for discharge. Figure 1 presents a schematic diagram of the wastewater treatment system.

The wastewater flows by gravity from the washing area to a collection sump of about 1,000 gallon (3.78 m^3) capacity. From this sump, the wastewater is pumped at an average rate of 15 gallons per minute (9.5×10^{-4} m^3/s) via a diaphragm-type positive displacement pump to an API separator located inside the treatment building. The API separator is 11.5 ft. (3.5 m) by 4 ft. (1.22 m) and contains a surface area of 46 square feet (4.3 m^2). In this unit, a baffled flow pattern and a detention time of 1-2 hours allows the free oils to float to the surface. The free oils are drained from the separator by gravity to an underground storage tank. Periodically, the oil is pumped from the storage tank to trailers and sold for re-refining.

Solids materials which settle in the API separator are periodically drained to a sludge storage tank. From the sludge tank, the material is drummed and shipped off-site for ultimate disposal in a licensed landfill.

Effluent from the API separator then flows by gravity to either of two 21,600 gallon (81.76 m^3) concrete storage basins. These basins serve as a means to collect the wastewater and also to provide a constant equalized feed to the remainder of the treatment process. Operation of the basins is such that while one basin is receiving wastewater from the API separator, the second is used as a feed source for the remaining treatment processes. Generally, this fill and draw cycle is alternated daily.

From the equalization tanks the wastewater is pumped via a centrifugal pump to a 500 gallon (1.89 m^3) flash mixing tank. A pH monitor in the pump discharge line prior to this mix tank measures the pH of the waste stream and proportions the feed of sulphuric acid to the tank to maintain a pH between 6.5 and 8.0. The mix tank also receives recycle water from the dissolved air flotation unit. Cationic polymer is added to this recycle water to effect the agglomeration of suspended solids. The cationic polymer solution is added at the rate of 0.02 (1.3×10^{-6} m^3/s) to 0.33 (2.15×10^{-5} m^3/s) gallons per minute via a chemical metering pump. The feed rate is determined by previous jar testing daily.

From the flash mixing tank, wastewater is pumped at the rate of about 100 gallons per minute (6.31×10^{-3} m^3/s) and delivered to a 2 ft. (0.61 m) Dia. x 5 ft. (1.5 m) high pressurized retention tank. Atmospheric air induced by means of an eductor into the suction side of the pump saturates the wastewater with dissolved air at a pressure of 40 psi (276 kPa). Flow of the wastewater from the pressure retention tank is controlled via a pressure control valve prior to introduction into a dissolved air flotation unit. Immediately following the control valve, an anionic polymer solution is added to the wastewater at the rate of 0.02 - 0.12 gallons per minute (1.3×10^{-6} - 7.6×10^{-6} m^3/s) via a second chemical metering pump. This polymer also also aids in the agglomeration of a suspended material such that the solids are more easily removed in the flotation unit.

The dissolved air flotation (DAF) unit is 8 ft. (2.4 m) diameter and 6'3" (1.9 m) high and provides an effective surface area of 40 $ft.^2$ (3.7 m^2). In the unit, the pressurized waste stream is released to atmospheric pressure in a center well. As the small bubbles of air form in the tank, suspended materials become attached and rise to the water surface. Here the froth is skimmed and stored in the sludge collection tank and later removed for off-site disposal. The heavier flocculated materials formed by the polymer addition settle to the bottom of the tank and are drained back to the batch equalization tanks. About 70% of effluent from the dissolved air flotation unit is recycled back to the flash mixing tank to aid in the solids removal process and to minimize cost of chemicals.

Treated wastewater from the dissolved air flotation unit is then fed to a 2,250 gallon (8.52 m^3) storage/feed tank for subsequent treatment. From this tank, wastewater is pumped at a rate of 30 gallons (1.9×10^{-3} m^3/s) per minute to a 4 foot (1.2 m) diameter mixed-media filter. This unit is filled with 18" (0.46 m) of a 0.4 mm sand and 18" (0.46 m) of 0.5 mm anthrafill. As the wastewater passes down through the mixed-media bed at a surface loading rate of 2 gpm/sf (1.36×10^{-3} $m^3.s^{-1}.m^{-2}$) residual suspended solids carried over from the DAF unit are removed. As solids are removed on the filter, a hydraulic pressure loss is experienced which necessitates backwashing of the media. The washing procedure is initiated at a pressure drop varying from 10-15 psi (69 - 102 kPa). Filter effluent is used for backwashing and is pumped from a holding tank upflow through the filter at the rate of 15 gpm/sf (0.01 $m^3.s^{-1}.m^{-2}$). The backwash water is then directed to the batch collection tanks at the head of the system for retreatment.

Effluent from the mixed-media filter then flows by pressure through two granular activated carbon fixed-bed adsorbers operated in a downflow mode, in series. Each adsorber contains 20,000 pounds (9072 kg) of granular activated carbon providing a contact time of about 175 minutes per bed. As the wastewater passes through these units, high molecular weight organic chemicals are adsorbed on the surface of the carbon. At the same time, low molecular weight organic materials pass through the unit for further treatment in a biological system. When breakthrough of organic material occurs in the lead carbon bed, wastewater flow is directed to the second adsorber and the exhausted carbon is replaced. The spent carbon removed from the system is returned to the supplier for reactivation. The freshly filled adsorber is then placed back on line in the second stage or polish position.

Effluent from the carbon adsorption system flows to a 3,000 gallon (11.4 m^3) surge tank and then to a rotating bio-filter (RBF) system. This unit combines the principles of the rotating bio-disc and the trickling filter bio-filtration systems. The unit is comprised of a 7.5 (2.3 m) by 6 ft. (1.8 m) cylindrical basket arrangement mounted on a horizontal axis and filled with 1-1/2" (3.81 cm) by 2" (5.0 cm) polyethylene rachig rings. A total of 212 cu. ft. (6.0 m^3) of media provides a total surface area of 1,400 square feet (130 m^2). As shown in Figure 2 , the system rotates in a 500 gallon (1.89 m^3) open tank partially filled with the wastewater.

A bio-mass develops on the media which is contacted with the wastewater as it rotates in the tank. This bio-mass biologically degrades organic materials remaining in the wastewater.

The effluent from the RBF unit flows by gravity into a 50,000 gallon (189.3 m^3) concrete holding tank. Water is then normally recycled from this tank through the RBF unit at a recirculation rate of 75-100%. Periodically, biological solids are pumped from the bottom of the effluent tank and returned to the batch collection tanks at the head of the system.

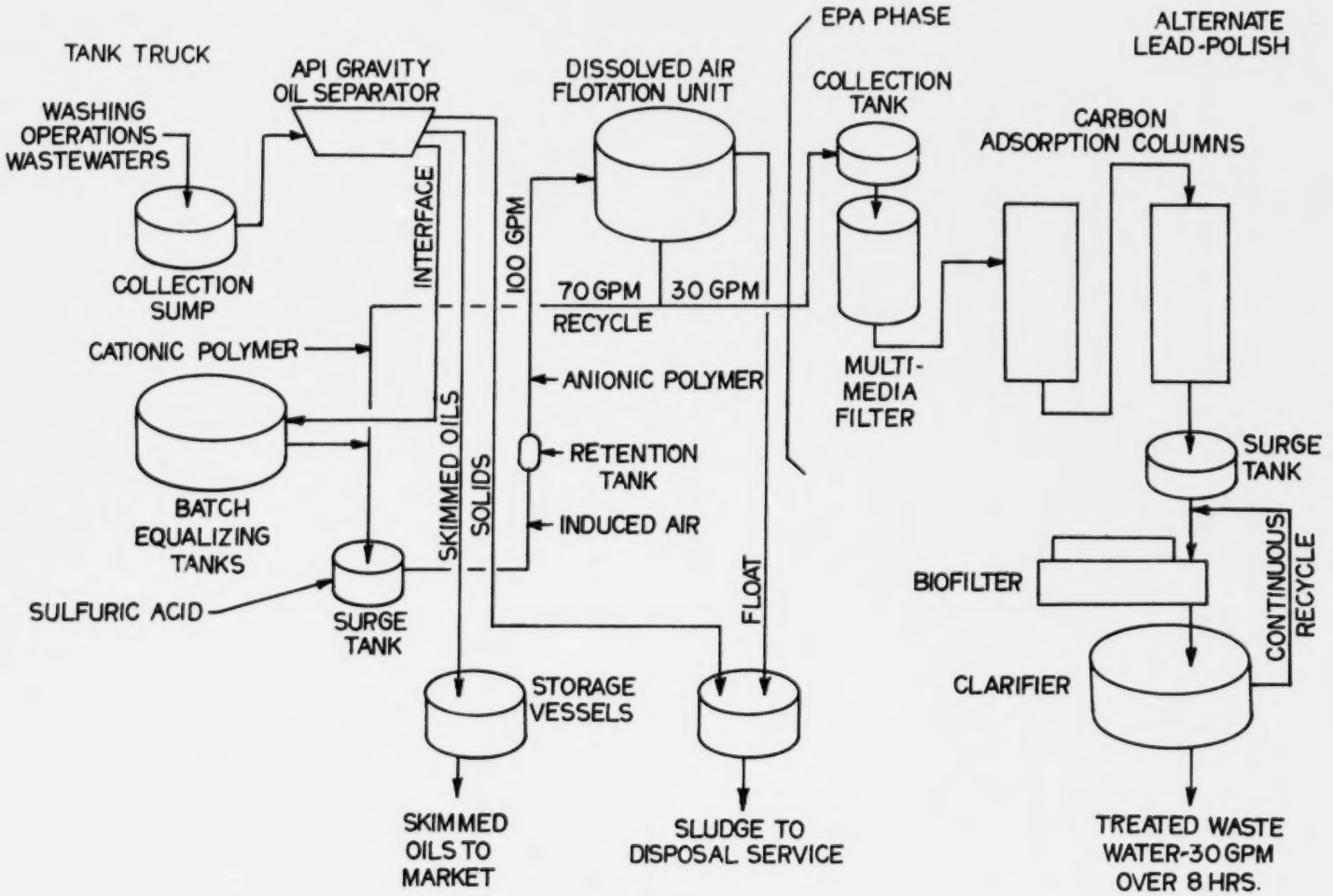


Figure 1. Flow Schematic.

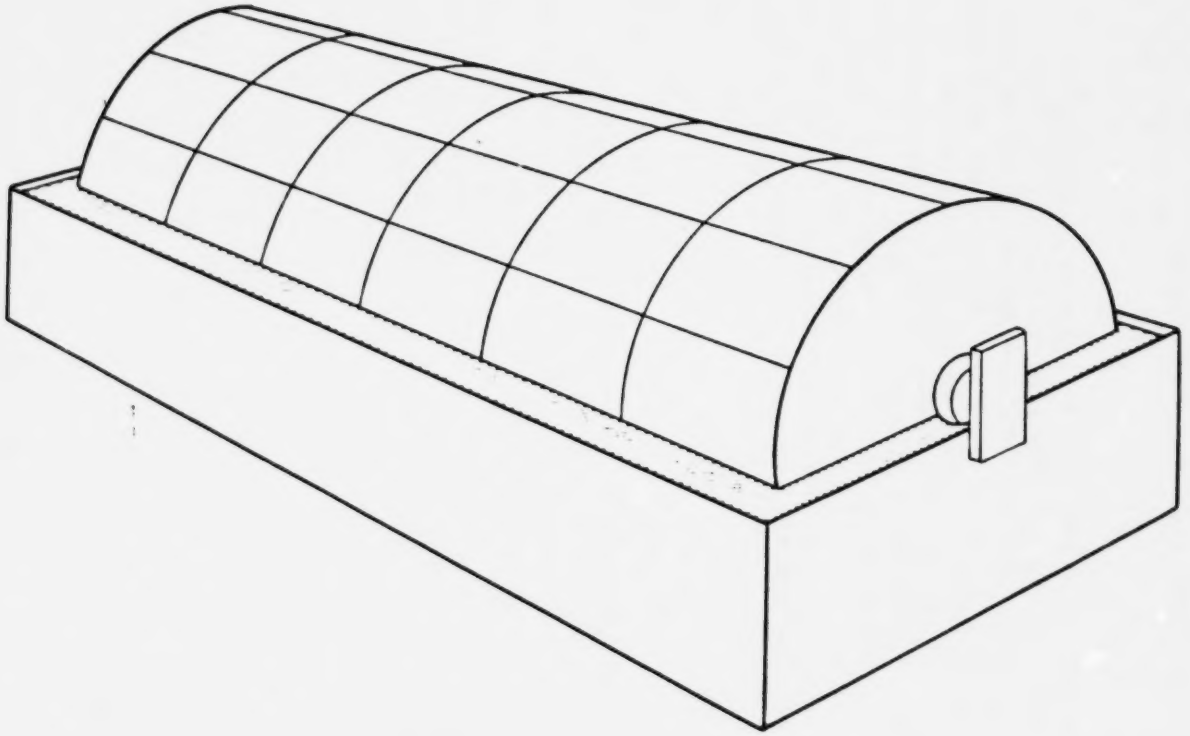


Figure 2. Rotating biofilter unit: continuously rotating cylindrical basket supports biological agents on raschig rings and provides continual rinsing of biological agents via half immersion in tank in which rotates.

SECTION 4

EXPERIMENTAL RESULTS AND DISCUSSION

GENERAL EFFECTIVENESS

A summary of the data collected from the tank truck washing wastewater treatment facility is presented in Table 2. Due to the intermittent nature of the washing terminal discharges, it was impossible to properly sample and analyze the raw wastewater. As such, the performance data for the treatment facility was generated across the dissolved air flotation, filtration, adsorption and bio-filtration treatment processes. Table 2, however, does present raw wastewater data characteristics which were determined by calculation using the oil and sludge removal data collected during operation. Overall, the treatment system averaged greater than 90% removal of COD. Oils and greases and phenolics were reduced by greater than 99%, averaging less than 1 and 0.1 mg/l respectively, in the system effluent.

API SEPARATOR

The API separator system employed at the head of the treatment sequence performed well over the demonstration period. On the average, 125 gallons (.47 m^3) of floating oils per operating day were removed and sold for re-refining at the rate of 5¢ per gallon. The system also generated a total of 80 gallons (0.3 m^3) of settable sludge per week at a solids concentration averaging 8%. The sludge was collected and drummed in 55-gallon (0.2 m^3) steel containers and hauled off-site for disposal in an approved landfill. Effluent from the API separator averaged 400 mg/l oil and grease.

NEUTRALIZATION

Prior to chemical coagulation, pH reduction from 10 - 12 to 6.5 - 7.5 was automatically controlled. An average of 5 gallons (0.02 m^3) of 66° Be' sulfuric acid were consumed in this process per operating day.

DISSOLVED AIR FLOTATION (DAF)

Both cationic and anionic polymer were added to the DAF feed to effect proper floc formation. The cationic polymer (Magnafloc 509C) was added first, at an average concentration of about 600 ppm. This was

TABLE 2. SUMMARY OF TREATABILITY DATA FOR PERIOD 2/10/76 - 6/23/77

	Wastewater	API separation/ dissolved air flotation	Mixed-media filtration	Carbon adsorption		Biofiltration
				Lead carbon	Polish carbon	
pH	10.5 - 12.5	10.5 - 12.5	6.5 - 8.0	6.5 - 8.5	6.5 - 8.5	6.5 - 8.5
Color APHA	Over 500	Over 500	50 - 100	1 - 10	1 - 5	10 - 50
Turb JTU	Over 500	Over 500	5 - 30	5 - 10	1 - 5	--------
COD mg/l	1,800 - 15,000	1,800 - 11,500	1,100 - 5,500	900 - 1,900	650 - 1,800	125 - 1,500
BOD_5 mg/l	600 - 3,000	600 - 2,200	--------	800 - 1,500	550 - 1,300	20 - 800
O & G mg/l	110 - 600	110 - 375	5 - 15	----------	<1	<1
Phenols mg/l	1 - 500	1 - 260	1 - 200	----------	0.1	0.1
SS mg/l	300 - 5,000	100 - 1,300	10 - 20	----------	0.1	--------

followed by the addition of an anionic polymer (Magnafloc 835A) at an average concentration of 8 ppm.

The DAF system generated about 750 gallons (2.8 m^3) of sludge (10% solids) per day requiring off-site disposal. Effluent from the flotation unit averaged 3,500 mg/l COD, 100 mg/l oil and grease and less than 100 mg/l suspended solids.

It was imperative that batch collection tanks be provided for equalization in order to operate the dissolved air flotation process properly. Even with this technique, the raw waste emulsion could not be broken on several occasions. This usually resulted when there was an inadvertant discharge of latex heels to the system or unusual successive cleaning of four or five tankers which carried this product. At these times, the excessive concentration of surfactants in the wastewater blocked flocculation reaction. Further, the pressurized wastewater when released to the atmosphere in the DAF overflowed the unit with foam. The operator was generally able to overcome this problem by placing the system on 100% recycle for several hours and/or returning the entire volume to the other batch holding tank, or increasing the cationic polymer dosage to the maximum feed rate.

Other than temporary shutdown for maintenance, the DAF system operated efficiently.

MIXED-MEDIA FILTRATION

The mixed-media filtration system received wastewater from the DAF system. The average pumping rate of 30 gallons per minute (1.89×10^{-3} m^3/s) provided a surface loading rate of 2.5 gpm/sf. (1.7×10^{-3} $m^3.s^{-1}.m^{-2}$). At this loading rate and an average suspended solids feed of less than 100 ppm, the filter contained sufficient capacity to allow about 5 operating days between backwashings.

A backwashing rate of 15 gpm/sf (0.01 $m^3.s^{-1}.m^{-2}$) was utilized for cleaning the filter system. A total of 2,700 gallons (10.2 m^3) of filtered water was required during the 15-minute backwash cycle. This water was directed to the head of the treatment facility for reprocessing.

The filter performed very well over the duration of the study. The suspended solids were reduced by approximately 90% and averaged about 10 mg/l in the effluent to the carbon columns.

CARBON ADSORPTION SYSTEM

The carbon adsorption system was utilized in the treatment scheme for the purpose of preferentially removing high molecular weight organics which may be toxic to a biological treatment system. Preliminary studies indicated a need for about 50 pounds (22.7 kg) of carbon per 1,000 gallons (3.79 m^3) of wastewater treated to remove the bio-refractory and bio-toxic organics. This requirement was essentially confirmed in the study as the full-scale systems utilized about 20,000 pounds (9072 kg) per month of activated carbon. It should be pointed out, however, that

the carbon beds were replaced based on monitoring of phenol in the carbon effluent. At this point, there was 1.0 mg/l phenol and, generally, approximately 2,000 mg/l COD. A reduction in the carbon usage rate might be expected if the system were monitored for breakthrough of other specific organics, if phenol were not present.

Phenolic compounds were consistently reduced by greater than 99% while the average COD removal was about 65% in the activated carbon process.

Table 3 displays representative water quality characteristics for a given month. Oil and grease, BOD, COD, and suspended solids were consistently reduced as a result of the system treatment. Figures 3 through 6 graphically show these results.

TABLE 3. TYPICAL INFLUENT AND EFFLUENT CHARACTERISTICS

	System Influent After Gravity Separation				System Effluent After Carbon Treatment			
Date	O & G	BOD	COD	SS	O & G	BOD	COD	SS
3/01/76	132	867	3140	536	<1	353	490	7
3/03/76	116	483	3880	630	<1	361	---	5
3/09/76	155	426	1480	407	<1	410	492	5
3/11/76	119	1140	4160	486	<1	435	536	1
3/18/76	256	560	3650	1280	<1	410	720	2
3/19/76	644	675	2520	1480	<1	344	670	1
3/23/76	553	815	3850	1300	<1	435	585	4
3/24/76	417	800	4190	987	<1	400	526	-

Table 4 shows the percent removal of oil and grease, BOD, COD, and suspended solids for the example month of March, 1976, that was calculated from Table 3.

TABLE 4. PERCENT REMOVAL OF TESTED PARAMETERS

DATE	% Removal O & G	BOD	COD	SS
3/01/76	>99	59.3	84.4	98.7
3/03/76	>99	25.3	----	>99
3/09/76	>99	3.8	66.8	98.8
3/11/76	>99	61.8	87.1	>99
3/18/76	>99	26.8	80.3	>99
3/19/76	>99	49.0	73.4	>99
3/23/76	>99	46.6	84.8	>99
3/24/76	>99	50.0	87.4	>99

Figure 7 graphically shows this data.

Concentrations of BOD and COD are important factors in determining the biological treatability of a waste stream.

BOD, which is the amount of oxygen consumed by aerobic bacteria while decomposing organic matter, is a vital test for determining oxygen requirements of an aerobic biological waste treatment process and becomes a means of predicting or observing the oxygen depletion in a natural stream resulting from waste discharge.

COD is a test that is also widely used as a means of measuring the pollution strength of industrial wastes. The test provides a measure of the oxygen consumed by organic matter that is susceptible to oxidation by a strong chemical oxidant.

Therefore, BOD tests indicate how much biodegradable organic material is in the waste and the COD test result includes the biodegradable and what can be chemically oxidized. Since BOD measures only the organic material that is biodegradable and COD measures all organic material, the BOD:COD ratio is an indicator of the biological treatability of wastes.

Table 5 lists the BOD:COD ratios for the equalized influent after gravity separation and effluent from the activated carbon during a typical month. The higher BOD:COD ratio for the carbon effluent is a direct result of the aforementioned systems and indicates a higher degree of biological treatability. Figure 8 is a graphical representation of the data.

TABLE 5. BOD/COD RATIOS

Date	System Influent After Gravity Separation	System Effluent After Carbon Treatment
3/01/76	0.276	0.720
3/03/76	0.124	-----
3/09/76	0.288	0.833
3/11/76	0.274	0.812
3/18/76	0.153	0.569
3/19/76	0.268	0.513
3/23/76	0.212	0.744
3/24/76	0.191	0.760

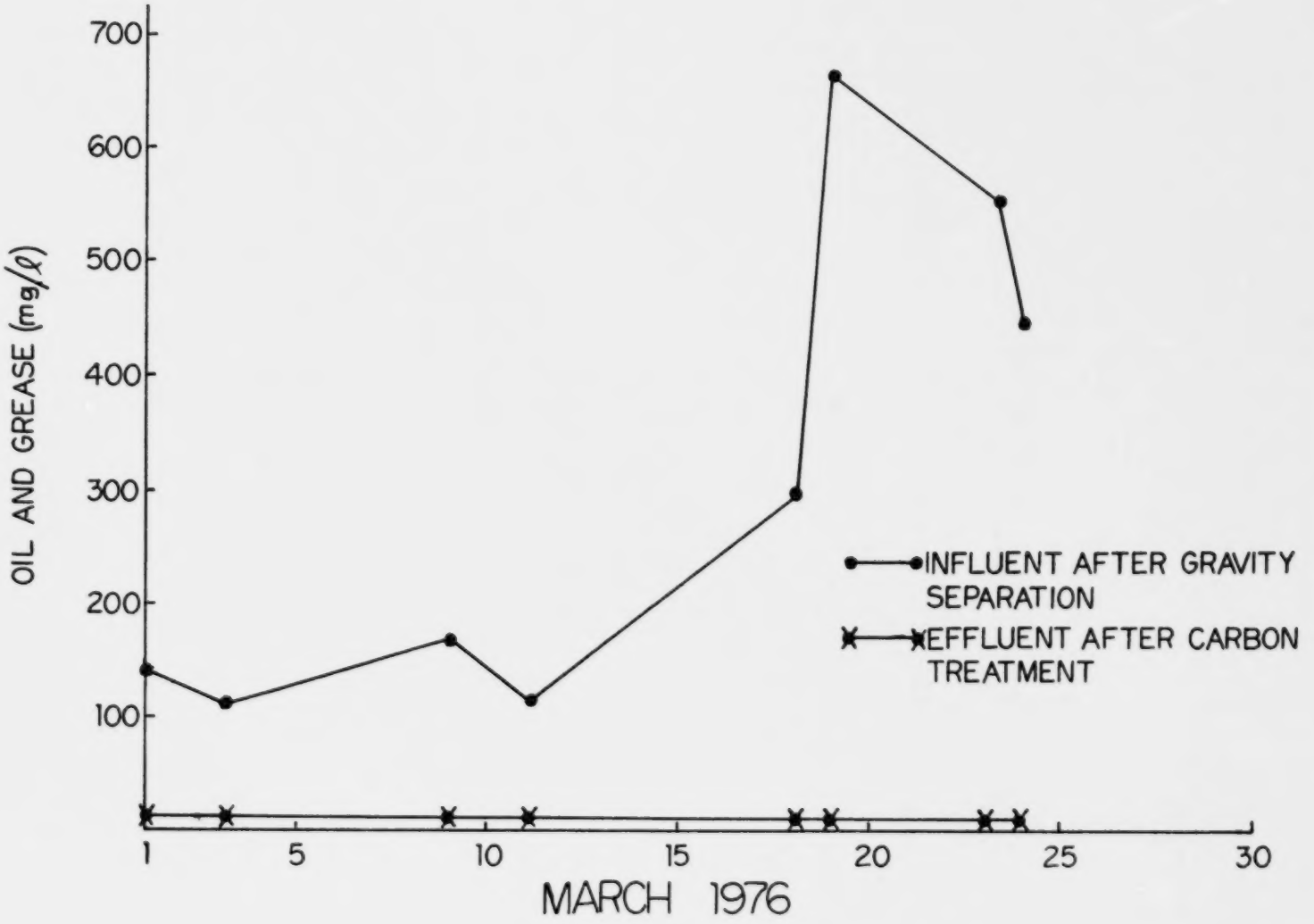


Figure 3. Influent and effluent oil and grease measurements.

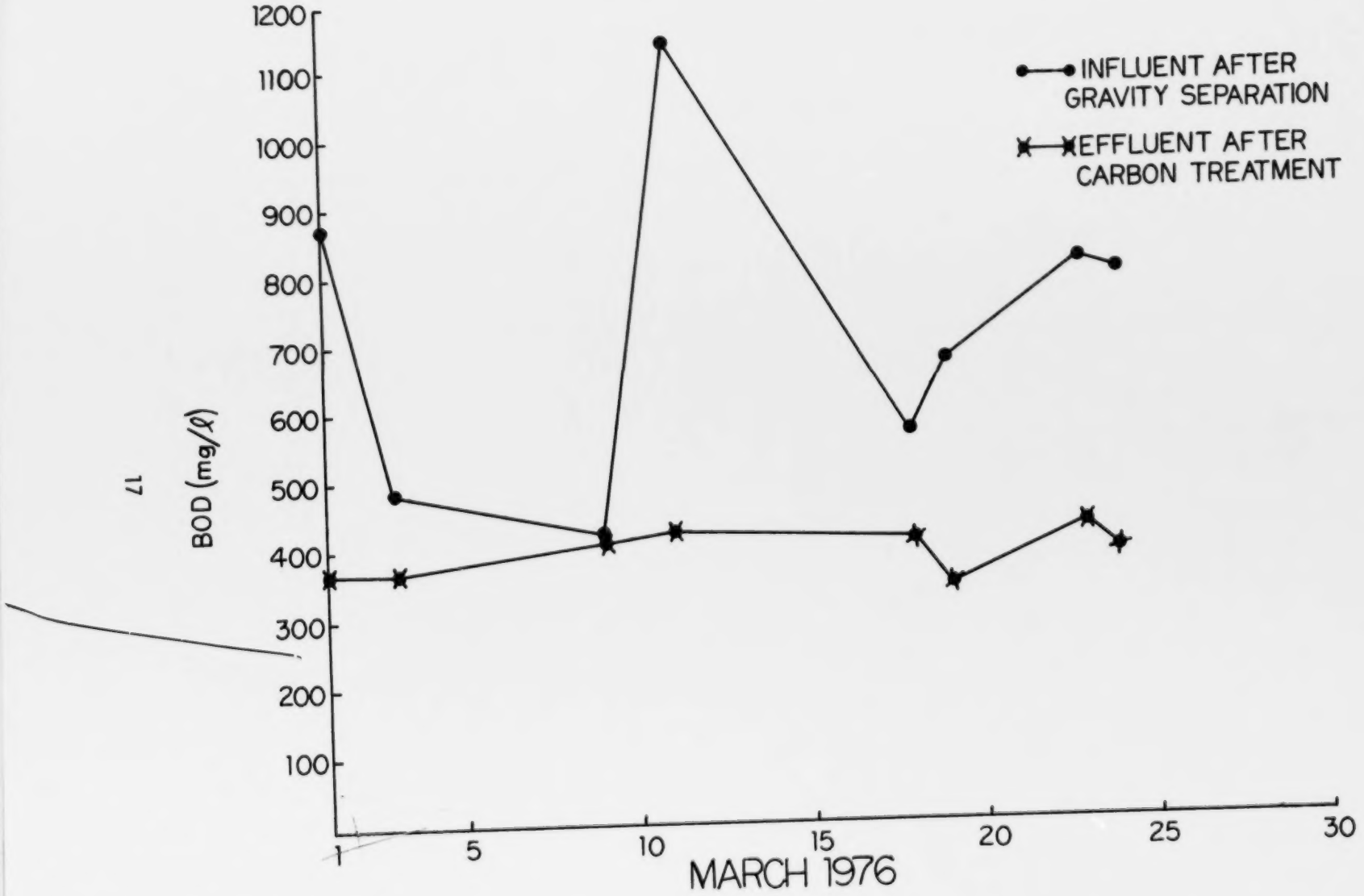


Figure 4. Influent and effluent BOD measurements.

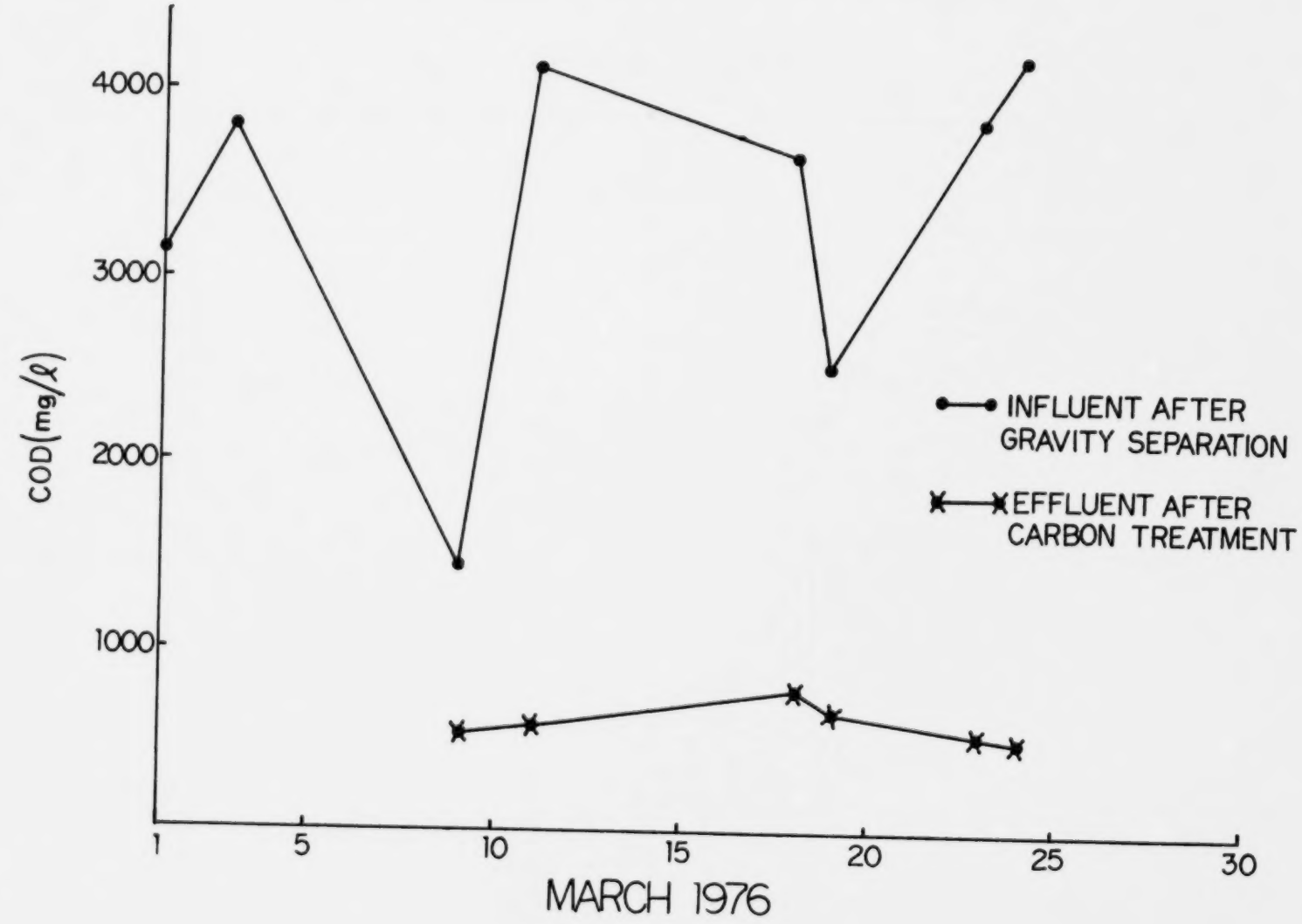


Figure 5. Influent and effluent COD measurements.

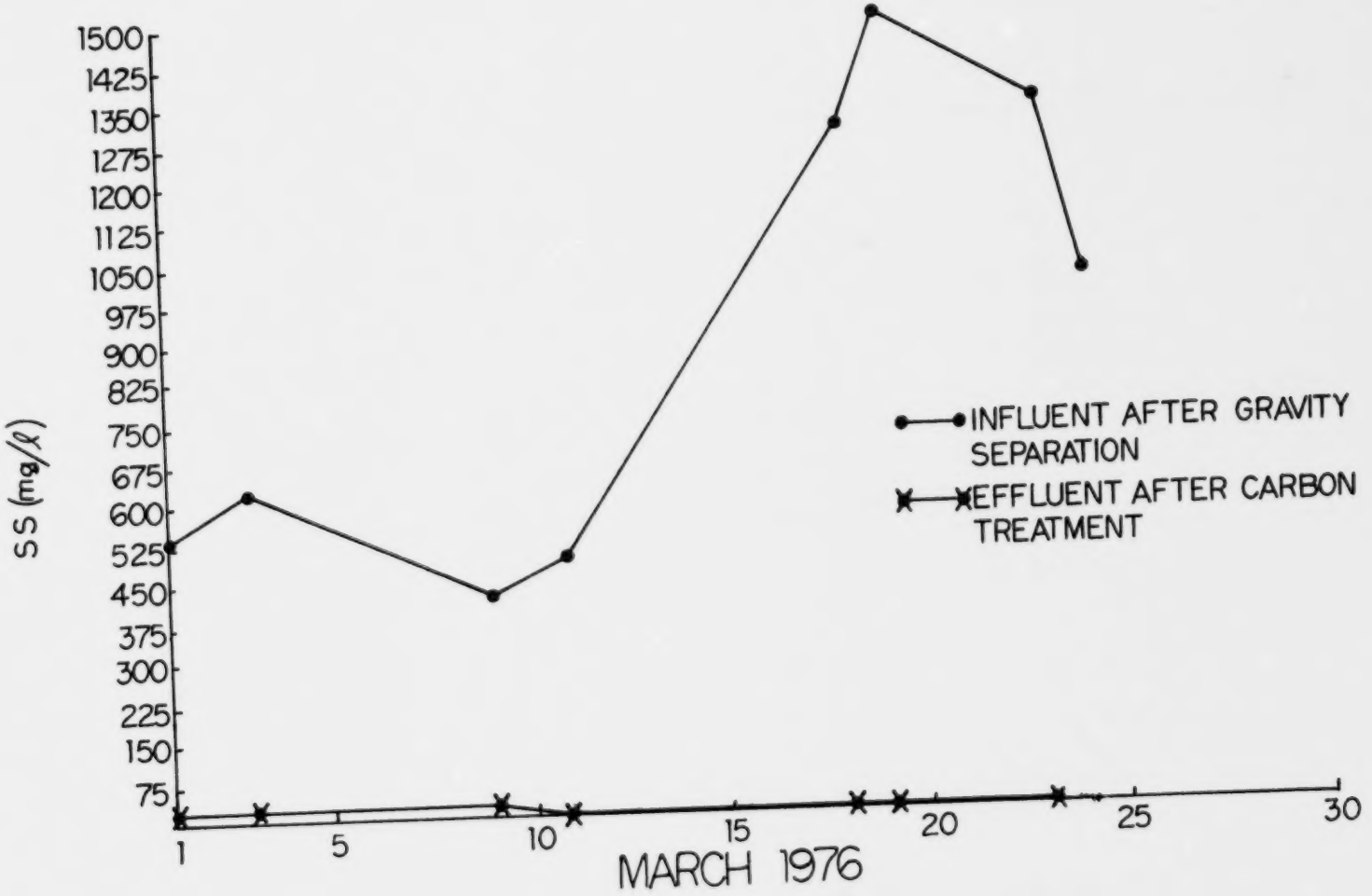


Figure 6. Influent and effluent SS measurements.

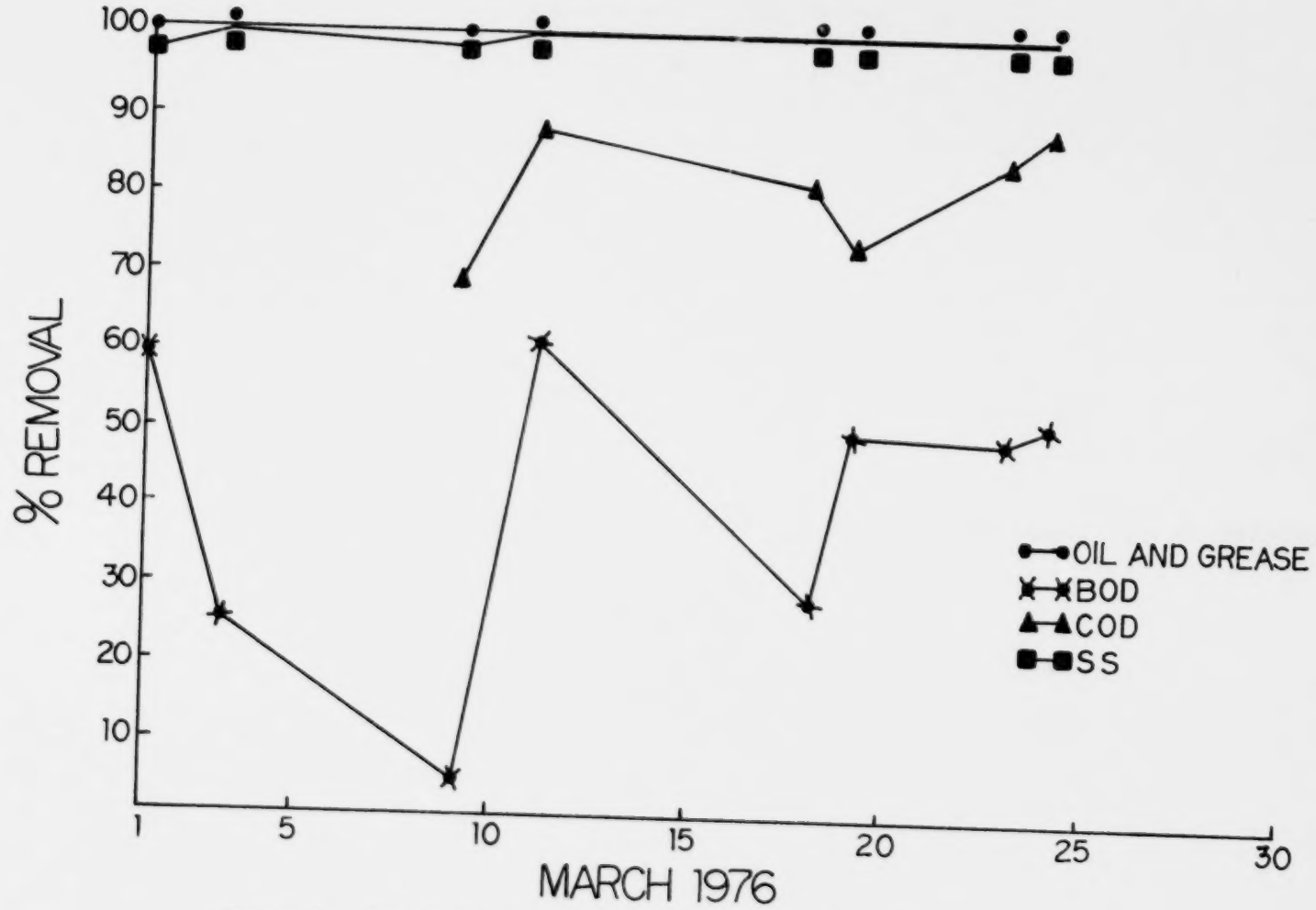


Figure 7. System treatment removal of O & G, BOD, COD, and SS

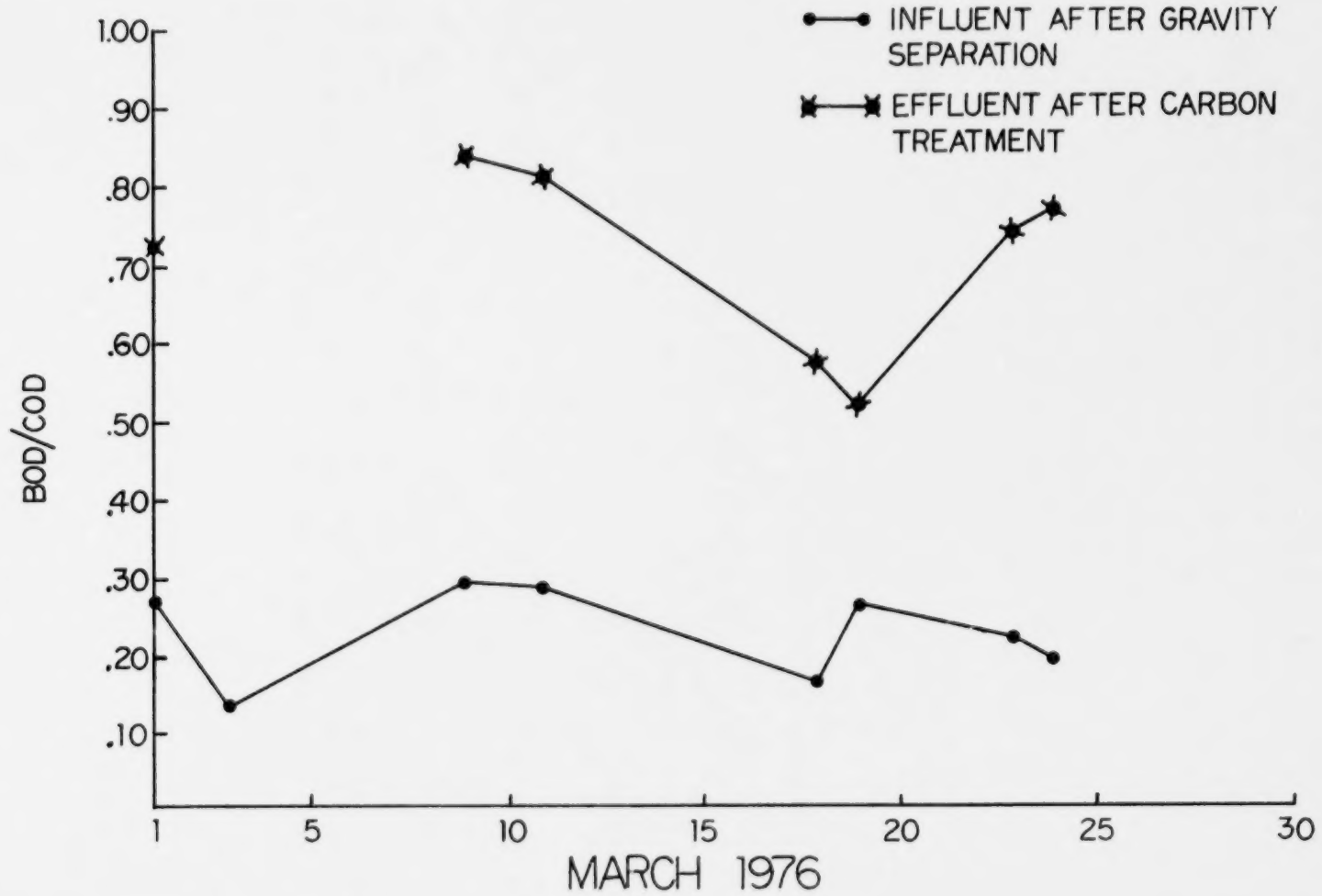


Figure 8. Influent and effluent BOD/COD ratios.

Further substantiation of the carbon system's ability to remove bio-toxic organics was the actual operating experience. During the study, the biological system was never upset or poisoned despite the known presence in the raw influent of several bio-toxic or bio-refractory organics. The only problem experienced with respect to the carbon adsorption system was the tendency of the packed beds to turn septic during periods where the system was not run or when abnormally high surfactant loadings were experienced. The cause of the septic condition was traced to the growth of anaerobic bacteria within the carbon beds. These bacteria reduced sulfur compounds present in the cleaning agents which were adsorbed on the carbon to the sulfide state which generated hydrogen sulfide gas. This problem was overcome by soaking the carbon beds in a dilute (5%) caustic solution to kill the sulfur reducing bacteria.

Even when the septic conditions were experienced, no adverse effects on the treatment capability were noticed. The sulfide compounds produced in the carbon beds were apparently oxidized down stream by the dissolved oxygen in the feed to the biological system.

ROTATING BIOLOGICAL FILTER (RBF)

It was evident very early in the study that the RBF biological system was undersized for the application. This severe overloading of the bio-system with soluble organics resulted in an inability to maintain dissolved oxygen concentration in the bio-filter tub. During ideal periods, however, when feed from the physical/chemical system was reduced and the wastewater was continuously recycled through the RBF from the final holding basin, the BOD was reduced to less than 30 mg/l.

Short circuiting of wastewater across the RBF tub was also observed, and this most certainly resulted in insufficient contact between the wastewater and the bio-mass.

Several experiments were tried to overcome these problems, and to permit continuous feed from the carbon adsorption system. Additional compressed air was bled to the RBF tub on several occasions. It appeared, however, even when sufficient dissolved oxygen was available in the RBF tub, the contact time was too short to permit acceptable levels of removal to be achieved, when treating the full flow of 15,000 gpd. (6.6×10^{-4} m^3/s).

In a second experiment, the bio-mass which was sloughed off the RBF rachig rings was filtered from the wastewater in the tub via a continuous recycle loop. This proved somewhat effective in maintaining dissolved oxygen under periods of low loading. However, it was not effective under higher loading conditions.

The RBF unit operated on a 24-hour basis recycling wastewater from the effluent holding basin. Since the physical-chemical part of the system operated only about 8 hours per day, this gave an additional 16 hours of contact to the biological system. Utilizing this procedure, it was possible to reduce the effluent BOD levels to an average 200 mg/l.

It is estimated that the RBF unit employed in the treatment system was undersized by about a factor of 3 to 5. Expansion of this unit or substitution of some other biological treatment technology would have been necessary to achieve effluent BOD results consistently less than 20 mg/l.

CHEMICAL REQUIREMENTS AND SLUDGE GENERATION

The chemical requirements for ongoing operation of the system are presented in Table 6. The three primary chemicals used were sulfuric acid for pH adjustment and cationic and anionic polymers for flocculation of suspended solids.

Table 7 provides a summary of the sludge quantities generated from the various unit processes. A total of 830 gallons (3.14 m^3) of sludge were removed from the system daily. In addition, 125 gallons (0.47 m^3) of oil were removed from the API separator.

TABLE 6. SUMMARY OF TREATMENT SYSTEM CHEMICAL REQUIREMENTS

Chemical	Use	Quantity
Sulfuric acid	pH Adjustment	65 lbs/day (29.5 kg)
Polymer		
a) Magnafloc 509C	SS Coagulation	100 gal/day (4.4×10^{-6} m^3/s)
Magnafloc 835A	" "	1 lb /day (0.45 kg)

(*) American Cyanamid Company

TABLE 7. SUMMARY OF SLUDGE QUANTITIES GENERATED AT THE SWEDESBORO TREATMENT PLANT

Sludge	Quantity	% Solids
API Oil overheads	125 gal/day (5.5×10^{-6} m^3/s)	N.A.
API Sludge underflow	80 gal/day (3.5×10^{-6} m^3/s)	8
DAF Sludge overheads (a)	500 gal/day (2.2×10^{-5} m^3/s)	10
DAF Sludge underflow (a)	250 gal/day (1.1×10^{-5} m^3/s)	10

(a) Sludges generated in the rotating bio-filter were recycled and collected in the dissolved air flotation system.

ECONOMIC EVALUATION

The cost for operation of the wastewater treatment facility are summarized in Table 8. The costs are presented in 1977 dollars and are broken down into costs per operating day and per 1,000 gallons (3.79 m^3) of wastewater treated.

TABLE 8. SUMMARY OF OPERATIONAL ECONOMICS

	In dollars	
	Cost/day	Cost/1,000 gals. (3.79 m^3)
Operating Costs - Total	$ 541.55	$ 36.10
Labor(a)	73.93	4.93
Carbon reactivation	256.41	17.09
Carbon makeup	52.88	3.53
Chemicals	57.69	3.84
Sludge disposal(b)	38.46	2.56
Power	11.54	.76
Maintenance	16.03	1.06
RBF	34.61	2.30
Capital cost	192.30	12.82
Depreciation 8 yrs. 10%	192.30	12.82
TOTAL COST	$ 733.85	$ 48.92

(a) One full-time hourly operator, 5-day, 9-hour day.
(b) 6.25¢/gallon (3.79×10^{-3} m^3) of sludge removed.

Due to rental of the filtration, adsorption and rotating biological filter systems at the Swedesboro facility, capital costs for these components were estimates only. The cost estimate presented assumes all the equipment would be capitalized and depreciated over an eight-year period assuming a 10% interest rate. This would bring the total capital cost for the facility to about $346,000.

On an average basis the cleaning of 30 trailers per day, six days per week generated about 500 gallons (1.89 m^3) of wastewater per unit on a total of 15,000 gallons per day. The treatment cost at $733.85 per day calculates to $24.46 per unit cleaned or $48.92 per 1,000 gallons (3.78 m^3).

Since the biological unit used in this study did not perform up to expectations, some additional costs associated with the expansion of this unit or for substitution of an alternate technology would be expected.

An additional study was conducted as a follow up to the initial work conducted under EPA Grant S803656-01. Although the results of the original study demonstrated that biological treatment of the truck cleaning wastewater following activated carbon treatment is feasible, the conclusion reached was that further development work was necessary to obtain a more compact process to reduce the final discharge to an acceptable concentration. Therefore, the decision was made to pilot test a two stage Hy-Flo (TM) fluidized bed system using anaerobic and aerobic modules. This Hy-Flo (TM) system is a proprietary process developed by Ecolotrol, Inc., Bethpage, New York.

SECTION 5

FLUIDIZED BED BIOREACTOR

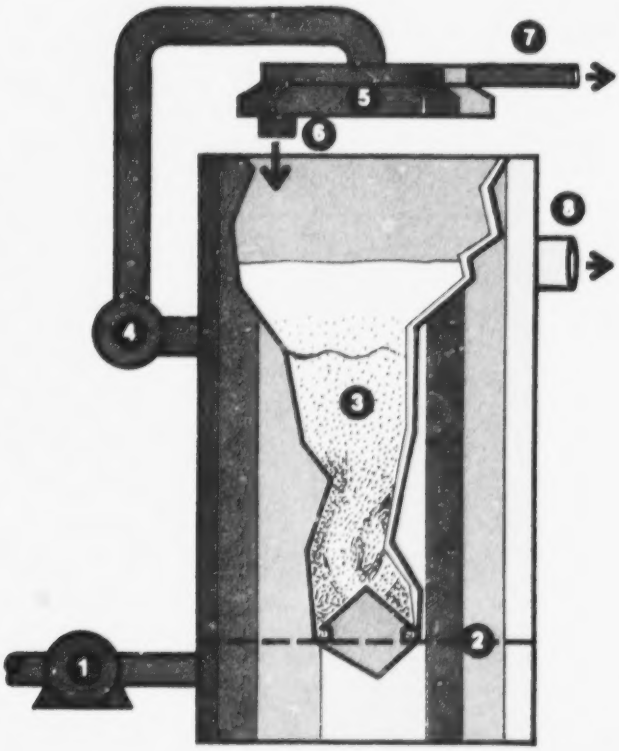
GENERAL DESCRIPTION

The Hy-Flo fluidized bed system illustrated in Figure 9 consists of a bioreactor partially filled with a fine grained media, such as sand. By passing the wastewater upward through the bottom of the reactor, motion is imparted to the media which serves to "fluidize" it. Once the sand is expanded in this manner, it presents a vast surface area for biological attachment. In time, a biological slime appears on the surface of the media and eventually covers the particles with a firmly attached, active biomass which effectively consumes the contaminants in wastewater as it passes by. In this way, the organisms are held "captive" in the reactor as in trickling filtration. The fluidizing of the media results in biomass concentrations which are an order of magnitude greater than conventional activated sludge systems as well as allowing intimate contact between the biological population and the wastewater. This allows treatment time to be drastically reduced as well as reducing the bioreactor volume by as much as 90%. As in trickling filters; the fixed biomass eliminates the need for sludge recycle to maintain the mixed liquor concentrations. However, the trickling filter has no provision for solids control within the reactor, and therefore requires a clarifier to remove any solids which have "sloughed off" the media and which otherwise would increase the effluent BOD_5 and suspended solids concentrations above the levels of secondary treatment. The fluidized bed system employs a positive mechanism for particle size control which eliminates the requirement for secondary clarification following the bioreactor.

As the biological slime thickness increases on the particle, its effective size is increased while its specific gravity decreases. For this reason, as the particle size increases, the bed expands accordingly. As the bed reaches its design maximum level, ultrasonic detectors in the reactor detect the bed level and automatically activate the sludge wasting system. A portion of the bed is pumped from the reactor, the excess sludge mechanically removed from the media, and the cleaned sand returned to the fluidized bed. This serves to lower the bed height which in turn deactivates the control system. Excess sludge removed in this manner is contained in a sidestream of approximately 1-3% solids. This volume of sludge is approximately 0.1-1.3% of the forward flow.

It is important to note that the Hy-Flo fluidized bed technology utilizes the same biology and chemistry indigenous to conventional biological waste treatment systems. The key to the success of process is the high concentration of microorganisms maintained within the reactor. These organisms can be any of the faculative, aerobic, or anaerobic bacteria typically found in a treatment system.

Due to the nature of the wastewater as shown in Table 5, it was decided to test the feasibility of anaerobic treatment followed by aerobic treatment as a polishing step. It was planned to utilize an anaerobic module to remove approximately 40-60% of the influent COD, with the effluent from the anaerobic module serving as influent to an aerobic module. This would serve to reduce cost for aeration in the aerobic system, as well as producing methane gas, a useable by-product, in the anaerobic mode. In order to evaluate the performance of each system and collect the necessary design parameters, the testing program was set up to allow parallel operation of the modules initially, with provision for series operation in the second phase of the study.



1. Influent Pump
2. Distribution Plate
3. Fluidized Bed
4. Solids Control Pump
5. Solids Separation Device
6. Media Return
7. Waste Sludge
8. Effluent

Figure 9. Fluidized bed reactor.

PILOT PLANT OPERATIONS

On June 15, 1977, the anaerobic pilot plant was delivered to the site and installed in the existing treatment building. Figure 10, depicts a typical module. The reactor was filled with a mixture of sand, seeded growth, and screened anaerobic digestor supernatent to aid in start-up. At the onset of testing, the anaerobic pilot was operated on a fill and draw basis withdrawing a portion from the unit daily and replacing it with an equal volume of fresh feed. In addition, since the initial wastewater characterization had indicated a nutrient deficiency, a source of nitrogen was added on a continuous basis. Adequate phosphorus was present for treatment. Alkalinity was provided to serve as a buffer against possible pH depressions caused by the buildup of volatile acids during the initial seeding period. As the production of methane increased, the system produced its own buffering capacity and the amount of sodium bicarbonate fed to the unit was decreased. The pilot plant was operated in this mode for several weeks until mid-August when it was decided that the system would function more efficiently using continuous feeding as opposed to the fill and draw mode. Within two weeks of the conversion, the unit was removing 75% of the influent COD, well above the 40 to 60% target. The unit was fed in this mode through September. This data is summarized in Table 9 .

The aerobic module was delivered and installed on July 19, 1977. As with the anaerobic system, additional nitrogen was supplied for synthesis, but no additional alkalinity was required. Pure oxygen gas was supplied to support the cellular metabolism of the aerobic micro-organisms.

This system was first operated in parallel with the anaerobic unit. During this period of operation, various combinations of loading rates and recycle ratios were investigated in order to formulate design parameters and maximize process efficiency. Removal efficiency averaged between 80 and 90%.

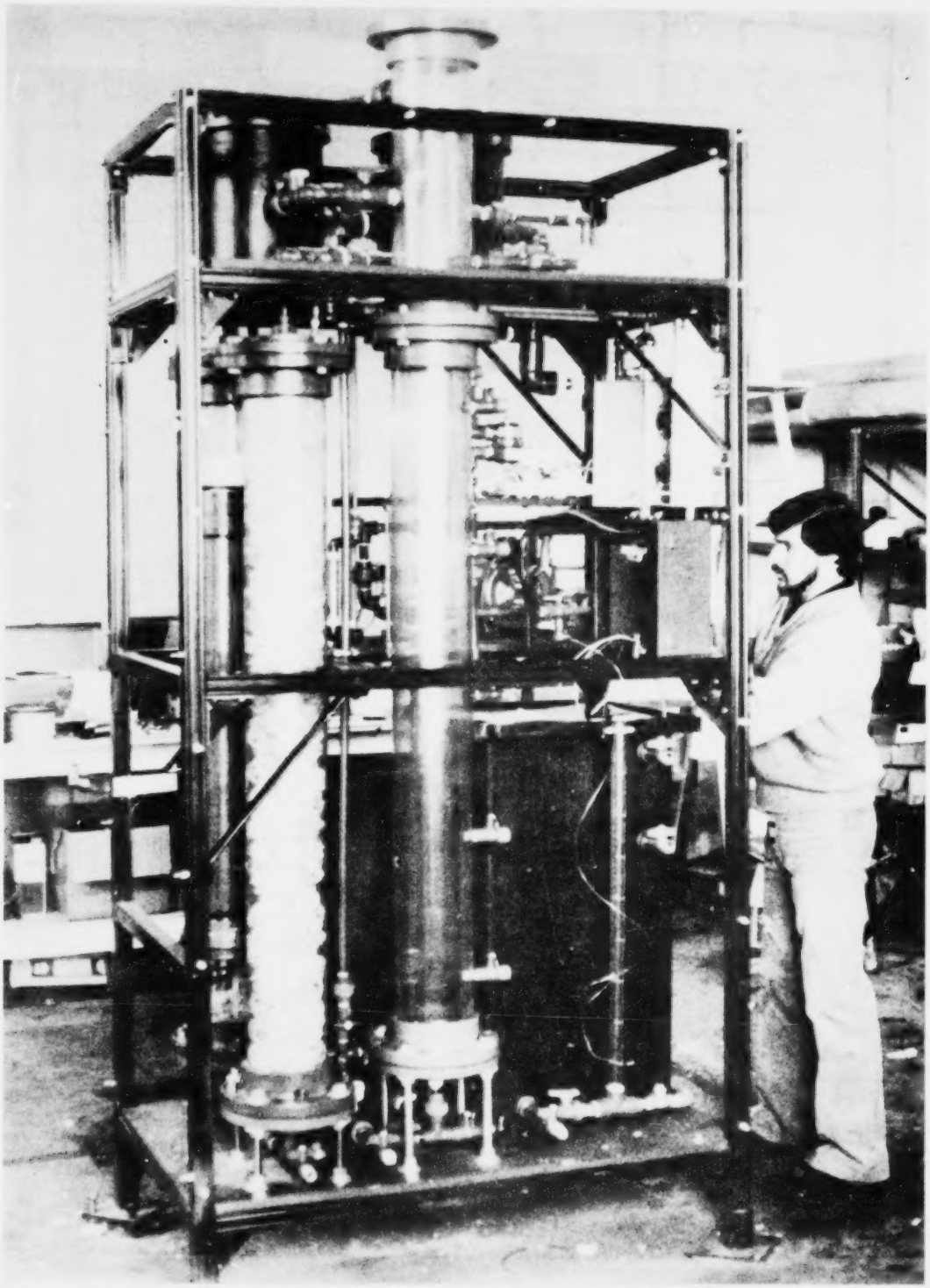


Figure 10. "Typical Hy-Flo ™" pilot plant being readied for shipment.

TABLE 9. MATLACK, INC. - SWEDESBORO TERMINAL

ANAEROBIC PILOT PLANT

(8/23/77 - 9/30/77)

Average influent COD	1680
Average effluent COD	433
% Removal	74%

TABLE 10. MATLACK, INC. - SWEDESBORO TERMINAL

SERIES OPERATION

NOVEMBER, 1977

Average TOC influent	482
Average effluent	42
% Removal	91%

SERIES OPERATION

After sufficient design data had been collected and analyzed for the two systems operating independently, the modules were placed in series for a period of three weeks. The loading rates and recycle ratios were set to provide about 50% removal in the anaerobic stage, with final polishing taking place aerobically. The results obtained in series operation substantiated the preliminary design parameters obtained from parallel operation. The anaerobic system operated at a design loading rate of 400 #COD/100 ft^3 per day for this period.

The aerobic stage provided the final polishing to accomplish a total average removal of 91% across the two units. The data for this period is presented in Figure 12 and Table 10.

Anaerobic digestion and methane utilization are by no means new developments in wastewater treatment. However, long detention times and large reactor volumes are generally required for adequate treatment efficiency and stability of operation. Since the growth kinetics of bacterial strains responsible for methane formation are very slow, detention times of 10 - 15 days are employed in digesters to prevent washout of the organisms. With this in mind, the fixed film approach of the fluidized bed becomes an attractive alternative to conventional suspended growth anaerobic reactors for BOD/COD removal.

Since the biomass in the fluidized bed is held "captive" on the media, the requirement for long detention times to prevent washout is eliminated. Hence the use of higher loading rates and reduced reactor size is possible in the design of the fluidized bed system.

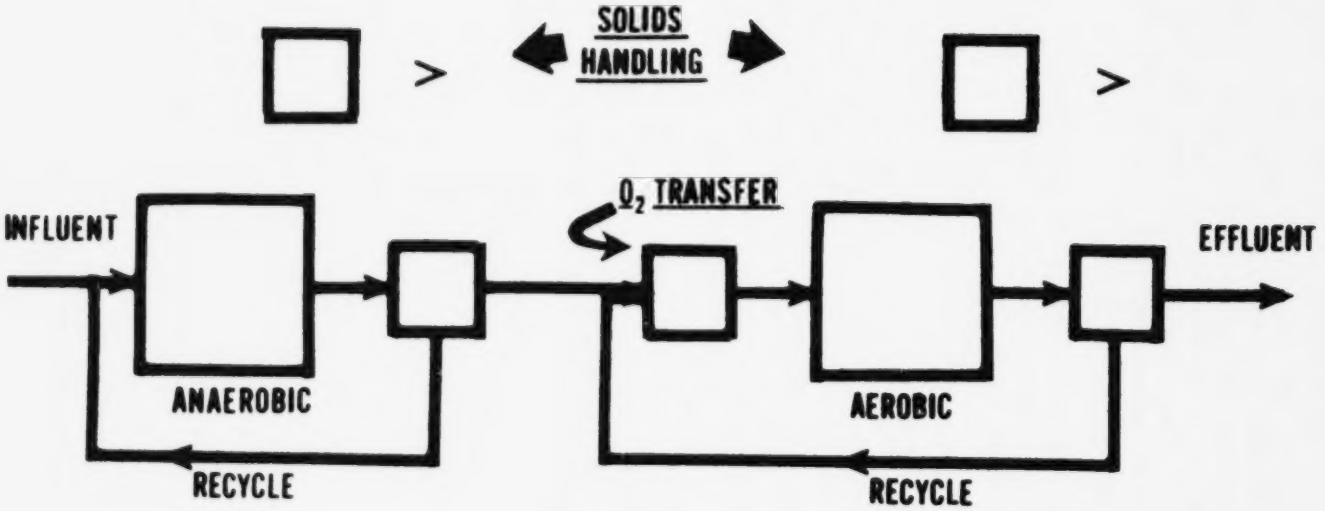


Figure 11. Process flowsheet.

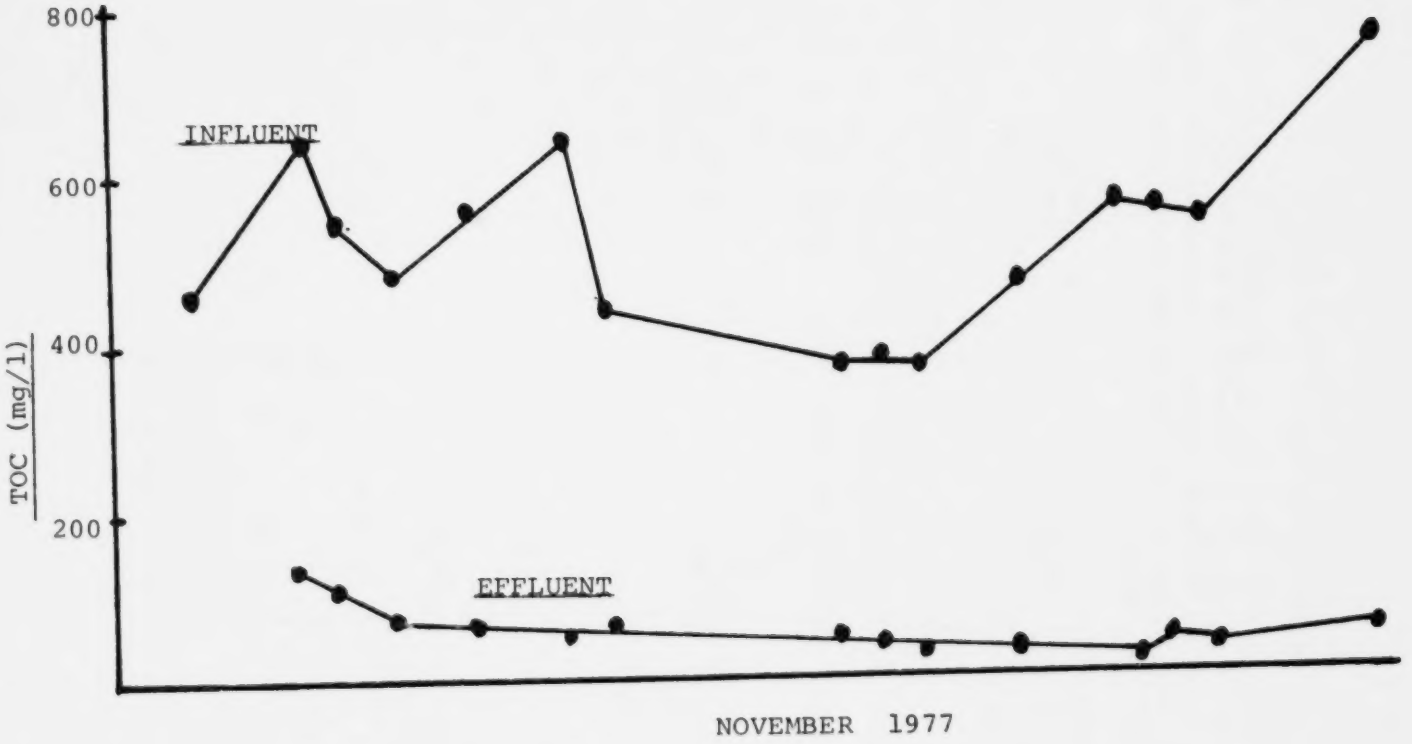


Figure 12. Series operation; Matlack pilot plants.

SECTION 6

TOXIC SUBSTANCE INVESTIGATION

The second phase of the study was to determine quantitatively the presence or absence of compounds of interest to the EPA and to subsequently evaluate the treatment system effectiveness for removal of these materials. The list of the 65 Consent Decree (a) compounds was used for the screening process.

Using the dispatcher's records at the Matlack, Swedesboro terminal, it was evident that many products were hauled for which there existed only minimal identification. Commodities, for example, might be labeled as plasticizer, resin, latex, etc. Many of these compounds were expected to contain some of the chemicals on the list, but the records available did not so indicate. From these records, a list was compiled of cargo most likely to contain these substances and the frequency of which they were hauled. Table 11 presents the identified shipments.

(a) Consent Decree, Train vs. NRDC, et al. June, 1976.

TABLE 11. SHIPMENTS SUSPECTED OF CONTAINING TOXIC CHEMICALS

Shipment identification	Loads per month
naphthalene	20
carbon tetrachloride	10
benzyl chloride	10
para nitro phenol	6
ortho nitrochlorobenzene	6
freon (dichlorodifluoromethane)	5
ammonium thiocyanate	10
boron trifluoride ether	5
toluene	4
benzene	6
phenol	3
plasticizer	10

Samples of the products listed in Table 11 were then collected from the product remaining in the tankers prior to cleaning. These products were delivered to a contractor's laboratory for the purpose of establishing reference standards.

Wastewater grab samples were then collected at five sampling points in the treatment system on several occasions. The sampling points included:

1. Effluent from the API separator
2. Effluent from the equalization tanks
3. Effluent from the sand filter
4. Effluent from the activated carbon
5. Effluent from the biological filter

Analyses were conducted through the use of gas chromatography using a Gowall Model 320 with flame ionization and electron capture detection capabilities. Typical detection sensitivity on this instrument ranges from 1 to 100 ppb depending upon sample extraction technique and the detector used. In 1976, when this testing was being carried out, the EPA had not yet developed the protocol for GC/MS analyses for priority pollutants. The conditions of analysis are given in Table 12.

TABLE 12. GC TESTING CONDITIONS

GOWALL MODEL 320 WITH FLAME IONIZATION AND ELECTRON CAPTURE DETECTORS

Sample volume	500 ml
Solvent	Hexane (50 ml)
GC column	Carbowax 400/Porasil F
Column temperature	150°C
Carrier gas	Nitrogen

Results of the testing were inconclusive as none of the reference compounds could be detected after the API Separator. Only naphthalene and benzyl chloride were identified in the raw feed.

The GC results, however, did indicate the presence of several unknown organics in the various samples. This was evidenced by a series of unknown peaks. The number of unknown peaks were determined as shown in Table 13.

TABLE 13. UNKNOWN GC PEAKS FOUND IN WASTEWATER SAMPLES

Sample point	Peaks observed
API	11 - 20
Equalization tank	4 - 16
Sand filter	1 - 4
Activated carbon	0 - 1
Biological	0 - 1

As a second part of the toxic study, samples of spent carbon were shipped to the supplier's laboratory and extracted and subjected to gas chromatographic/mass spectrographic analysis. The conditions of analysis are given in Table 14.

TABLE 14. GC/MS TESTING CONDITIONS

FINNIGAN MODEL 3200

Sample	40 grams activated carbon
Solvent	(1) hexane - 60 ml (2) carbon disulfide - 60 ml
Columns	(1) 5 ft. 3% OV-17 10 ft. 3% OV-225
Scan temperature	70 - 220°C - 6°/min

Qualitative results of the testing, indicating the compounds identified, are presented in Table 15. This data clearly indicates the removal of a variety of organic compounds via carbon adsorption. The fact that these compounds could not be detected in the earlier work probably indicates they were present in the water samples in only very low concentrations or they were masked in the GC testing by more concentrated background materials.

TABLE 15. COMPOUNDS IDENTIFIED BY GC/MS

CHARACTERIZATION OF SPENT CARBON EXTRACTIONS

Compound	Molecular weight
1-butanol	74
dichlorobenzene	146
n-nonanal	142
2-methyl-2, 4-pentanediol	118
p-hydroxybenzaldehyde	122
benzyl alcohol	108
phenol	94
dipropylene-glycol-methyl-ether	148
dipropylene glycol	134
benzaldehyde	106
ethyl (trans-2-methyl-2-methyl-3-isopropylaziridinyl) acetate	185
phthalimide	147
phthalic acid	166
nonamide	157
2-(2-vinyloxyethoxy) ethanol	132
2-butoxyethanol	118
3, 3-dimethyl-2-butanol	102
allyl benzoate	162
2,2,4-trimethyl-1,3-pentanediol	146
tripropylene glycol	192
2,5-dimethyl-1-hexane	112
2,3-dichloroaniline	161
tripropylene glycol methyl ether	206
tripropylene glycol	192
1-sec-butoxy-2-propanol	132
1-isopropoxy-2-methyl-2-propanol	132
n-vinyl-2-pyrrolidone	111
1,5-hexadiene	78
1,6-heptadiene	92
xylene (isomer)	106
2-ethyl-1-hexanol	130
2,4-dichlorophenol	162
n-acetylbenzamide	163
o-hydroxbenzl alcohol	124
butyrolactam	85
chloroethylene	62
ethylbenzene	106
1-undecene	154
2,3-epoxy-2-methylpentane	166
3-methyl-1-hexanol	116
1,2,4-trithiolane	124
ortho & meta cresol isomers	108

SECTION 7

CHEMICAL OXIDATION PILOT STUDY

The project was amended on September 9, 1977 to study the technical and economic feasibility of chemical oxidation of dissolved organics in wastewater from tank truck cleaning.

Pilot-scale field experiments were conducted on actual wastewater using an ozone-UV process. Both batch and flow type tests were conducted using two constant stirred tank reactors, which were connected in series for flow tests. Experiments were conducted under a variety of conditions.

To remove the residual organics after the ozone-UV process, a polishing concept based on the carbon adsorption process was also briefly examined.

INTRODUCTION AND BACKGROUND

An earlier bench-scale field study was conducted during April - May, 1977 at Matlack's Swedesboro, N.J. terminal. This was sponsored by the General Electric-RESD Independent Research and Development Program. It was determined that ozone-UV would reduce the concentration of dissolved organics in truck washing wastewater to a significant degree.

The pilot-scale study was carried out at Matlack's Lester, Pennsylvania terminal, (located near the Philadelphia International Airport.

Tank truck interior washing operations generate one of the most complex and difficult-to-treat wastewaters. The materials hauled by tankers vary widely in character and often may be highly toxic. The wastewaters from tank truck cleanings reflect these characteristics in their highly and rapidly varying composition. The wastewaters contain high concentrations of oils and organics which may be free, emulsified, or dissolved, and suspended solids. The wastewater needs to be treated for removal of free oils and organics and suspended solids prior to treatment for dissolved organics.

In a full-scale treatment system at the Lester terminal, the influent wastewater is first stored in two holding tanks for equalization of flow and pollutant loadings. Free oils and other organics from the waste are removed using an API type separator. The separator effluent undergoes chemical flocculation and air flotation to remove suspended

solids and a portion of emulsified oils and organics. Flocculated effluent needs further processing to remove dissolved organics. For evaluation of the ozone-UV method to remove dissolved organics, which is the purpose of this study, a portion of the flocculated effluent was filtered through a small sand-filter to remove any remaining particulate material and was then fed to the ozonation reactors.

Data obtained show that detention time, mixing speed, influent waste concentration, and influent ozone concentration are primary process variables. Other process variables examined include gas flow rate, UV intensity, reaction temperature, and pH. Within the limits examined, their effects were overshadowed by large, rapid, and continuous variations in the influent wastewater.

CONCLUSIONS AND RECOMMENDATIONS

An analysis of the experimental data from batch and flow tests shows that performance of the ozone-UV process is affected primarily by the influent waste concentration, detention time, influent ozone concentration and the mixing speed. Based on the data obtained, it is concluded that the ozone-UV process can consistently remove 80 - 90% of the dissolved organics from tank truck cleanings.

Tests were also conducted to study the effects of ozone flowrate, pH, UV intensity, and reaction temperature. Under the experimental conditions and within the parameter limits examined, the effects of these variables were overshadowed by large, rapid, and continuous variations in the influent conditions.

The data obtained have been utilized to project the economics of a full scale process, 15,000 gpd capacity. Based on this analysis, operating cost for the ozone-UV process is estimated at $10-20/1000 gallons depending on the influent waste concentration.

In order to evaluate the effects of a continuously varying influent on the performance of the ozone-UV process and establish the process economics on a firm basis, full scale tests on an engineering prototype system over a longer period, say one year, are recommended.

Bio-oxidation experiments designed for additional removal of dissolved organics from a waste stream treated with the ozone-UV process and which utilized carbon as a substrate indicated that biological growth can occur on the substrate. Pilot scale tests are recommended to demonstrate the concept and develop process design requirements.

EXPERIMENTAL DESCRIPTION

A schematic of the overall test setup is shown in Figure 13 with a picture of the actual setup in Figure 14. The main features of the setup are two reaction vessels in which gas and liquid are contacted and a polishing carbon column. Ozone was generated from oxygen using a Welsbach generator (Model CL-51-F20L capacity 75 lb/day, 480 V, 100 A, 60/10).

Ozone-UV Test Setup

The reaction vessels basically consist of two stainless steel, cylindrical, covered tanks, each equipped with a variable speed motor-stirrer, 4 UV lamps, 4 gas diffuser plates, and wrapped around with heater coils. Each tank is 2 ft ID, (0.61 m); 6 ft high (1.8 m); (≈140 gallons (0.53 m^3) of total volume), has four symmetrically placed 2-1/2 inch (0.06 m) wide baffles placed along the wall, and is provided with inlets, outlets and sampling ports for liquid and gas streams. A detailed schematic of a reaction vessel is shown in Figure 15. For flow tests, the two reactor vessels were connected in series with a 2-inch (0.05 m) diameter pipe as shown in Figure 16. Liquid was pumped to the bottom of the first vessel and was transferred by gravity to the bottom of the second vessel. Liquid level in each vessel was monitored using a piece of transparent Tygon tubing connected to the bottom. All piping, valves, and fittings used in the setup were made of 316 SS. Reaction gases from the vessels were exhausted to the outside of the building using a 1-inch (0.02 m) PVC line. The exhaust line included a rotameter to facilitate gas flowrate measurement in each vessel.

The mixers for the reaction vessels were obtained from Mixer Equipment Company, Rochester, N.Y.; each was equipped with a 60-inch (1.52 m) long shaft and two 8-inch (0.2 m) diameter flat turbine blade propellers. The UV lamps were General Electric Model G64T6, 65 watt; each 62 inches (1.57 m) long and 3/4 inch (0.02 m) in diameter. Each lamp was placed in a quartz tube, approximately 1-inch (0.02 m) in diameter. The four lamp assemblies were placed symmetrically around the tank perimeter, each between two baffles and approximately 2-1/2 inches (0.06 m) removed from the wall.

Four porous ceramic disk diffusers, each ≈8 inches (0.2 m) in diameter, were placed in each vessel for dispersing ozone gas into the liquid. The diffuser disk had a recommended gas flowrate range of 1 CFM/disk, and were manufactured by Ferro Corporation, East Rochester, N.Y.

Each reaction vessel was wrapped with a 1500-watt nichrome wire beaded heater which was covered with a (0.16 cm) 1/16 inch thick asbestos cloth for insulation purposes.

The polishing column consisted of a 6 feet (1.83 m) long 3-3/4 inches (0.1 m) ID plexiglass column which supported a 55 inches (1.4 m) high bed of granular activated carbon (Darco, 4 x 12 grade; Atlas Chemical Company, Wilmington, Delaware).

Operating Procedure

The reaction vessels were operated on an 8 hours/day, 5 days/week basis while the polishing carbon column was operated on 24 hours/day, 7 days/week basis. Flowrates in the two subsystems were different, and enough ozonated effluent was prepared daily to ensure a steady supply to the carbon column overnight or over the weekend.

The feed stream for the reaction vessels was prepared by sand filtration of a portion of the flocculated effluent and was stored in holding tank # 2 (Figure 13).

The main task in the startup consisted of setting the desired gas flowrate in the two reactors which was accomplished with the help of various rotameters, pressure regulators, and pressure gauges located in the gas feed lines, on the ozonator, and on the oxygen tank (Figure 16). Next, the UV lamps were switched on and the ozone production was started. Finally, the liquid stream was started to be pumped into the reactor vessel and the carbon column.

The entire system except the carbon column feed pump was shut down at the end of the day. The generator and the reaction vessels were purged with oxygen for 10-15 minutes before shutting off the gas supply.

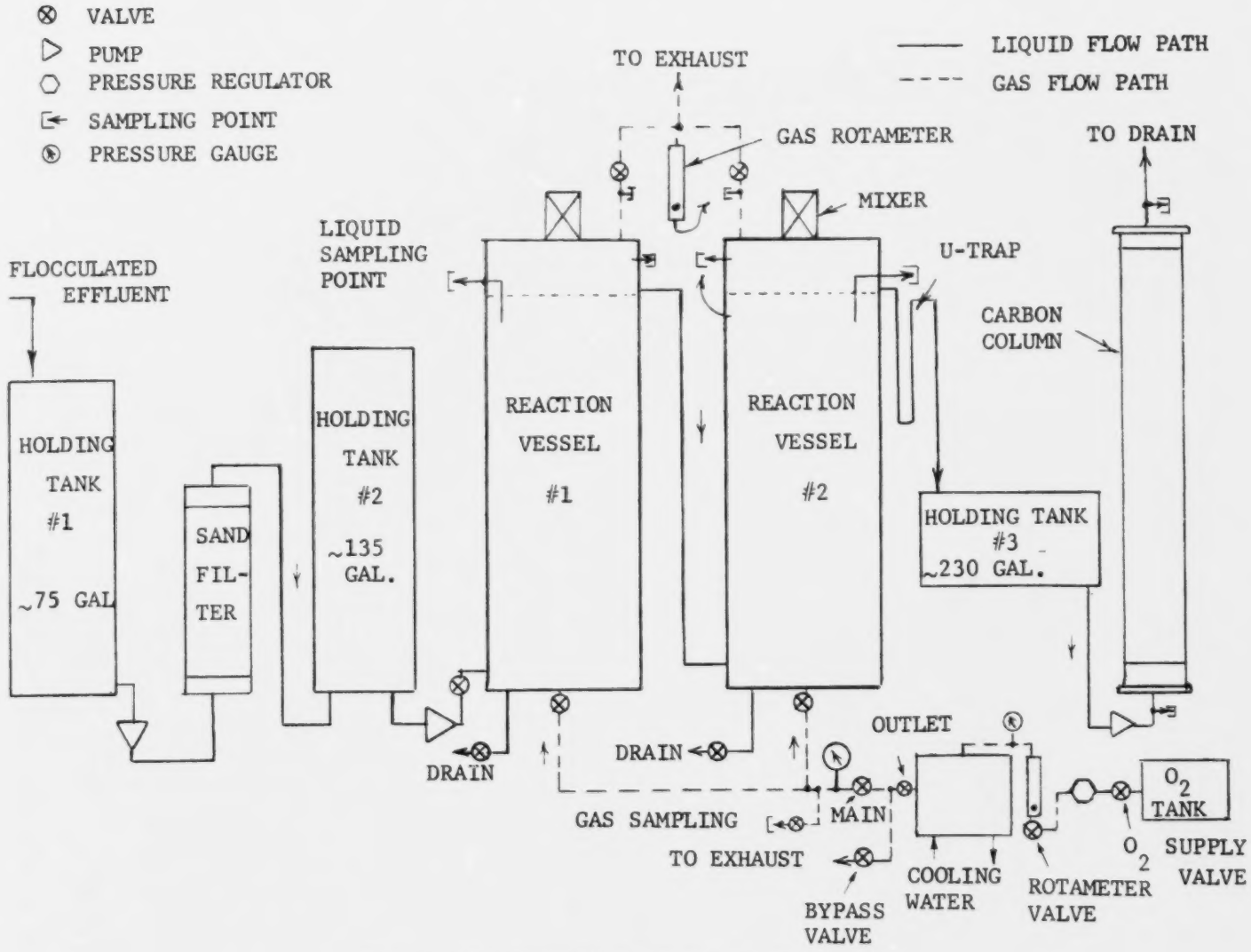


Figure 13. Overall test setup schematic.

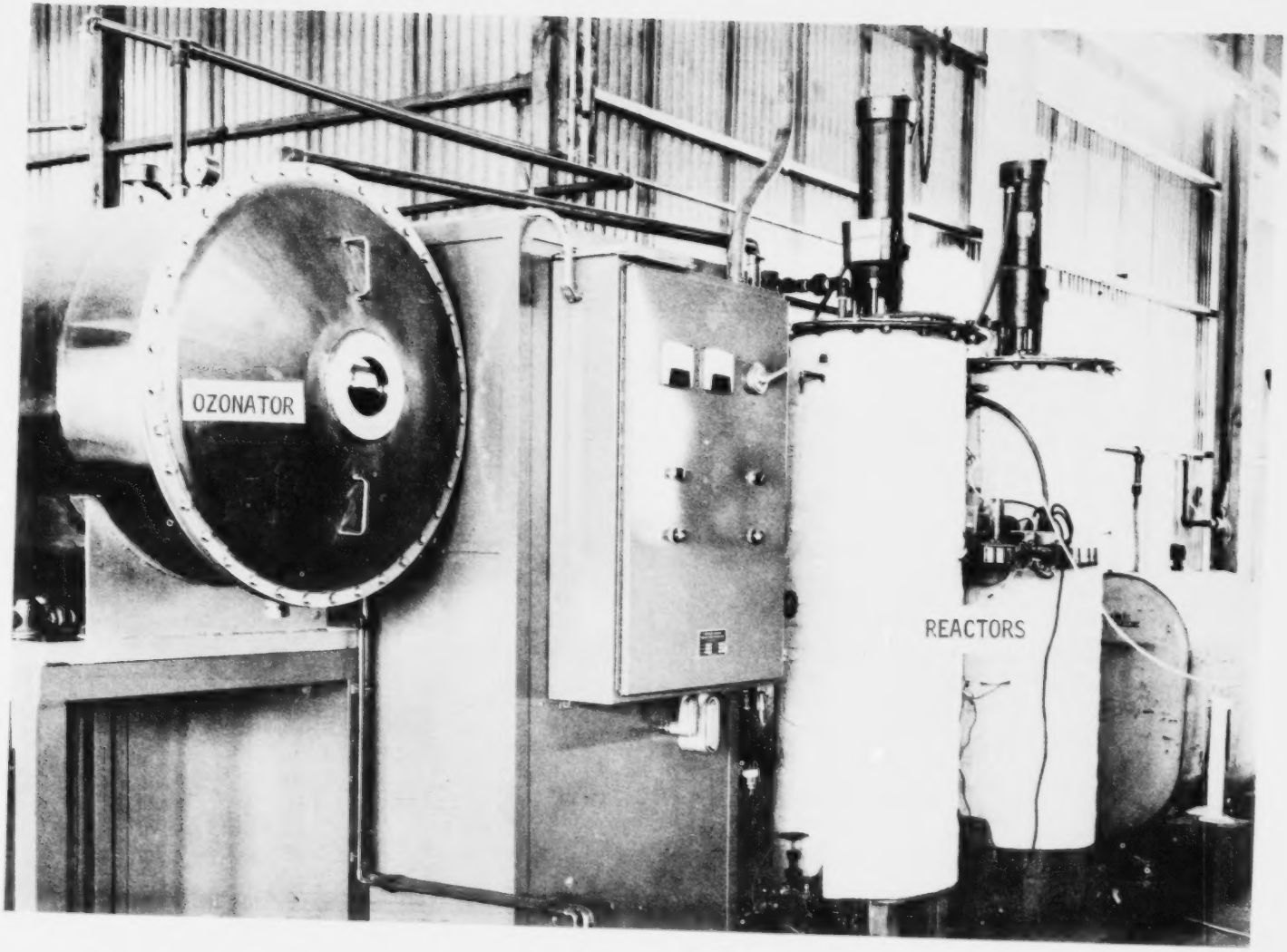


Figure 14. Actual test setup.

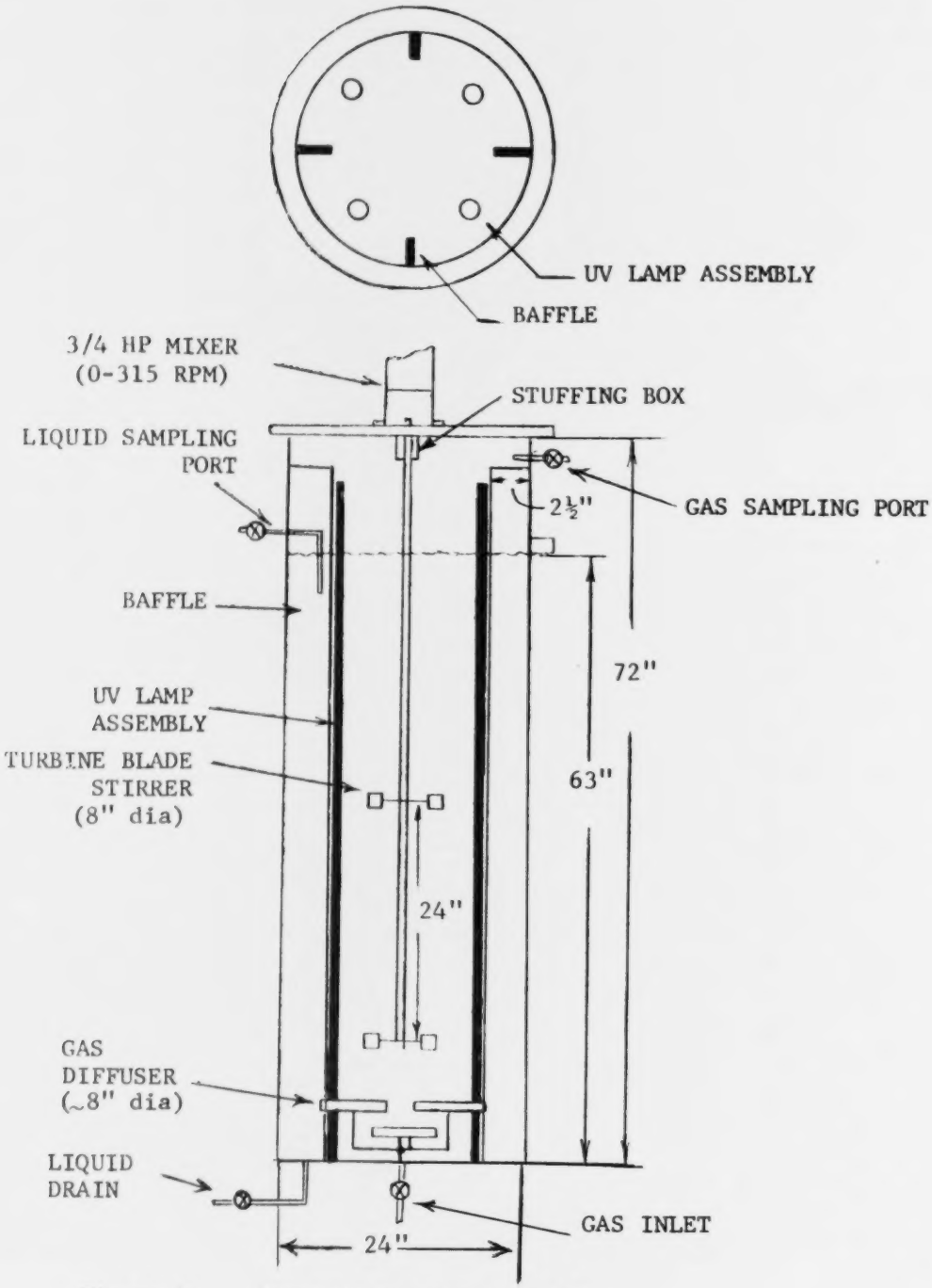


Figure 15. Ozone-UV reactor schematic.

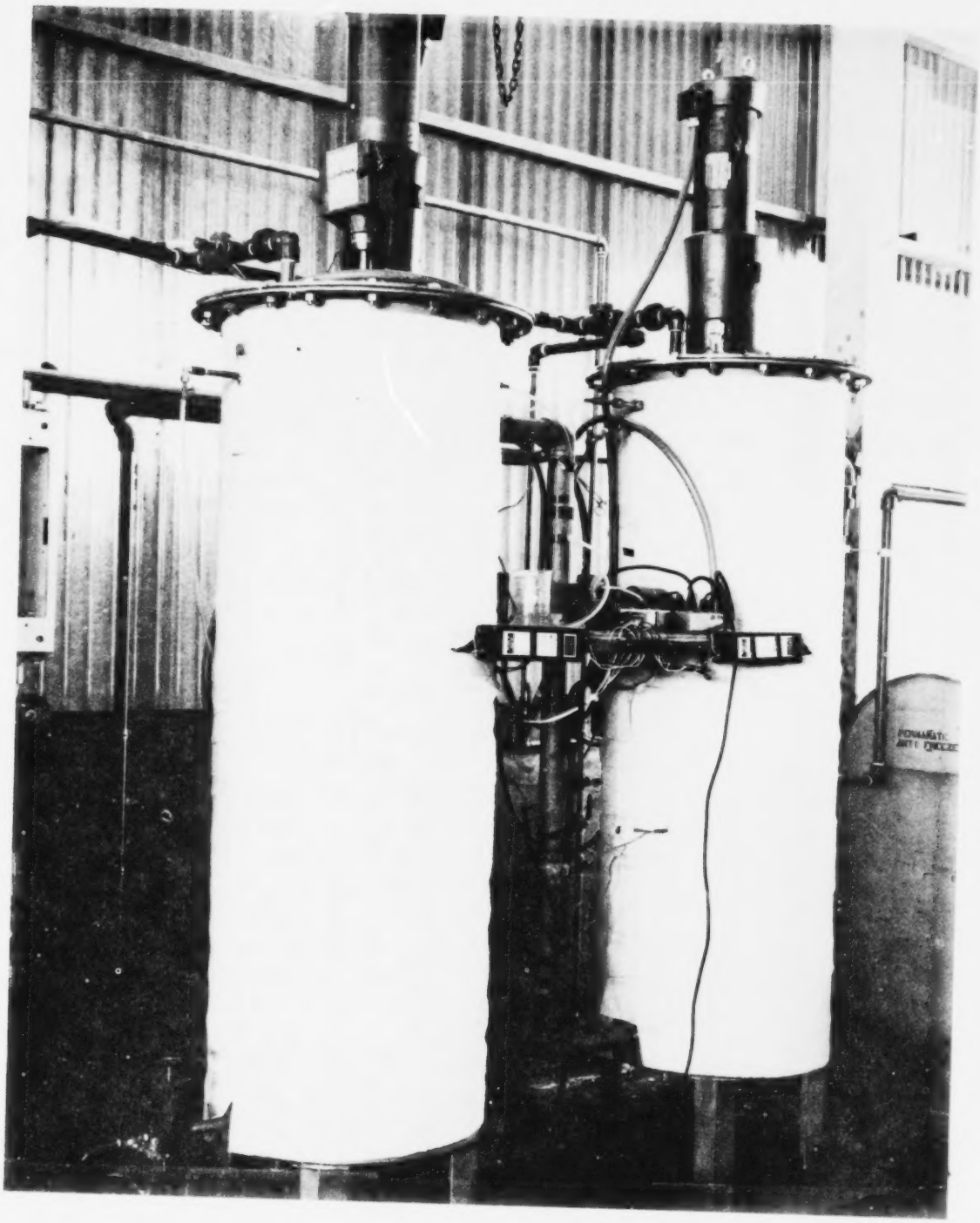


Figure 16. Two ozone-UV reactors connected in Series

Sampling and Analysis

Liquid Sampling and Analysis

Samples for analysis were taken every two hours on the influent to the first reaction vessels, the effluent from reaction vessels 1 and 2, the influent to the carbon column, and the effluent of the carbon column. Samples of influent to the first reaction vessel, and influent and effluent of the carbon column were composited. A liquid sample from each tank was withdrawn using a masterflex pump through the sampling port located on the side of the vessel near the top (Figure 15). The sampling tube was purged for a few minutes prior to collecting a sample.

Each sample was monitored for the pH using a Beckman Expandomatic pH Meter and for temperature using a 0-100^{o}C thermometer.

Liquid samples were analyzed primarily for organics concentrations; TOC, COD and BOD were used as monitoring parameters. TOC or TC (total carbon which was found to be almost the same as TOC) was used on a regular basis for all samples since the analysis is relatively more rapid and almost real-time for purposes of day-to-day experiment planning. COD was used on a selective basis and BOD even more selectively. TOC or TC measurements were made using a Beckman TOC Analyzer while COD and BOD measurements were made following Standard Methods procedures (COD and BOD measurements were supplied by Matlack).

Gaseous Ozone Concentration Measurement

Influent and effluent gases from each reaction vessel were monitored, usually twice a day for ozone concentration. Effluent gas was sampled from each reaction vessel through the gas sampling port located above the liquid level. Using a masterflex pump, gas was pumped through a 250 mℓ bubbler containing a 2% solution of potassium iodide. The bubbler was connected to a Wet Test Meter for gas flow measurement. After passing 1 liter of gas through the bubbler, the solution was quantitively transferred to a 250 mℓ beaker, acidified with 1.0N sulfuric acid and titrated with 0.1N sodium thiosulfate to obtain the concentration of O_3 in gas. In order to measure the O_3 concentration entering the reaction vessels, a gas sampling port on the inlet side of the vessels was used.

RESULTS AND DISCUSSION

Batch Tests Data

The overall objective of the batch tests was to determine process variables which are pertinent to the design of an ozone-UV process, evaluate relative sensitivity of the process performance to selected process variables, and utilize the data to design flow experiments. Tests were conducted under a variety of test conditions, including initial organics concentration in the wastewater, detention time, influent ozone concentration, mixing speed, UV intensity, and gas flowrate. Data from these tests are given in Tables 16-25 (included at the back of the report) and are also summarized in Figures 17 & 18. As mentioned earlier, the influent organics concentration varied over a wide range during these tests, being as high as 1885 mg/ℓ total carbon (TC) in run 6 and as low as 547 mg/ℓ TC in run 7.

An examination of the data in Figure 17 shows that detention time, influent ozone concentration, and mixing speed are the key process parameters. An increase in the influent ozone concentration (run 1 vs. run 5) or the mixing speed (run 2 vs. run 1) improves process performance tremendously. The process performance also appears to be more sensitive to mixing speed than UV. A doubling of the mixing speed (run 2 vs. run 1) is seen to be measurably more effective in reducing the organics concentration than doubling of the UV intensity (run 3 vs. run 1); furthermore, the effect of doubling the UV at high speed mixing is not appreciable at all as demonstrated by a comparison of runs 2 and 4. Under conditions of high mixing speed and high influent ozone concentration, a 100% increase in gas flow rate (run 6 compared to run 2) does not increase process effectiveness measurably. A reason for this may be that by doubling the gas flow rate in run 6, capacity of the diffuser plates was exceeded by almost 50% over the recommended limit by the manufacturer which could deteriorate the gas liquid contacting efficiency, for example due to an increase in the gas bubble size.

The effect of UV on the process performance was examined in runs 7 and 8, data for which are shown in Figure 18. For each run, the starting organics concentrations in the waste, measured as total carbon, for UV vs. no-UV runs were within 5-10% of each other. Data show that UV may enhance process effectiveness to a certain extent in some cases, but not always. This may be affected by, among other factors, the exact

TABLE 16. BATCH RUN DATA SHEET

Run #1

Date: 4/26-4/27

Voltage: 450V

Gas Flow Rate: 3 CFM

No. of UV Lamps Used: 2

Mixer Speed R.P.M.: 156

Time Hr.	pH	Temp. °C	O_3 Concentration Mg/liter		Total Carbon Mg/liter	TC Fraction Remaining	TOC Mg/l	TOC Fraction Remaining	COD Mg/l	COD Fraction Remaining
			Inlet	Outlet						
0	7.0	17			1312	1.00				
				10.1 (at 30 min)						
1	7.4	17		14.4	1288	0.98				
2	7.5	19	75.1	23.0	1212	0.92				
3	7.4	19			1175	0.90				
4	7.3	19	75.8	22.8	1112	0.85				
5	7.2	21			1025	0.78				
6	7.1	21		16.8	913	0.70				
7	6.8	21	78.4	23.5	875	0.67				
8	6.5	21			735	0.56				
9	5.8	21		38.6	650	0.50				
10	5.7	21		45.6	625	0.48				

TABLE 17. BATCH RUN DATA SHEET

Run #2

Date: 4/28/78

Voltage: 450V

Gas Flow Rate: 3 CFM

No. of UV Lamps Used: 2

Mixer Speed R.P.M.: 314

Time Hr.	pH	Temp. °C	O_3 Concentration Mg/liter		Total Carbon Mg/liter	TC Fraction Remaining	TOC Mg/l	TOC Fraction Remaining	COD Mg/l	COD Fraction Remaining
			Inlet	Outlet						
0	7.3	16			1350	1.00				
1	7.5	18			1287	0.95				
2	7.4	21	78.6	12.6	1200	0.89				
3	7.3	23			1062	0.79				
4	7.1	25		15.6	939	0.70				
5	6.8	27	75.8		863	0.64				
6										
7	5.8	31		32.6	675	0.50				

TABLE 18. BATCH RUN DATA SHEET

Run #3

Date: 5/1/78

Voltage: 450

Gas Flow Rate: 3 CFM

No. of UV Lamps Used: 4

Mixer Speed R.P.M.: 156

Time Hr.	pH	Temp. °C	O_3 Concentration Mg/liter		Total Carbon Mg/liter	TC Fraction Remaining	TOC Mg/l	TOC Fraction Remaining	COD Mg/l	COD Fraction Remaining
			Inlet	Outlet						
0	7.1	17			1325	1.00	1228	1.00		
1	6.7	18	78.0	0.9 (at 30 min.)	1250	0.94	1188	0.92		
2	6.7	20		36.0	1262	0.95				
3	6.8	21			1150	0.87	970	0.75		
4	6.8	22	77.8	37.7	1025	0.77				
5	6.8	23			925	0.70	881	0.68		
6	6.8	25		33.6	850	0.64				
7	6.8	25			750	0.57	752	0.58		

TABLE 19. BATCH RUN DATA SHEET

Run #4

Date: 5/2/78

Voltage: 450V

Gas Flow Rate: 3 CFM

No. of UV Lamps Used: 4

Mixer Speed R.P.M.: 314

Time Hr.	pH	Temp. °C	O_3 Concentration Mg/liter		Total Carbon Mg/liter	TC Fraction Remaining	TOC Mg/1	TOC Fraction Remaining	COD Mg/1	COD Fraction Remaining
			Inlet	Outlet						
0	7.3	15			1425	1.00	1250	1.00	4150	1.00
1	6.3	20		1.0 (at 30 min.)	1287	0.90	1240	0.99		
2	6.1	23	80.4	15.6	1200	0.84				
3	6.2	25			1150	0.81	970	0.78	2580	0.62
4	6.3	27	81.1	31.7	987	0.69				
5	6.2	29			875	0.61	855	0.68		
6	6.2	31			812	0.57				
7	6.1	-		30.7	712	0.50	674	0.54	1560	0.38

TABLE 20. BATCH RUN DATA SHEET

Run #5

Date: 5/3/78

Voltage: 272V

Gas Flow Rate: 3 CFM

No. of UV Lamps Used: 2

Mixer Speed R.P.M.: 156

Time Hr.	pH	Temp. °C	O_3 Concentration Mg/liter		Total Carbon Mg/liter	TC Fraction Remaining	TOC Mg/l	TOC Fraction Remaining	COD Mg/l	COD Fraction Remaining
			Inlet	Outlet						
0	7.1	18	25.7		1525	1.00	1270	1.00	4190	1.00
1	7.5	19	44.6	1.7 (at 30 min.)	1462	0.96	1270	1.00		
2	7.5	20		9.4	1460	0.96				
3	7.6	20	31.2	9.4	1400	0.92	1190	0.94		
4	7.5	22			1348	0.88				
5	7.5	-	36.5	11.3	1312	0.86	1140	0.90		
6	7.5	22	34.5	14.4	1292	0.85	1120	0.88	3450	0.82

TABLE 21. BATCH RUN DATA SHEET

Run #6

Date: 5/5/78

Voltage: 450V

Gas Flow Rate: 6 CFM

No. of UV Lamps Used: 2

Mixer Speed R.P.M.: 314

Time Hr.	pH	Temp. °C	O_3 Concentration Mg/liter		Total Carbon Mg/liter	TC Fraction Remaining	TOC Mg/l	TOC Fraction Remaining	COD Mg/l	COD Fraction Remaining
			Inlet	Outlet						
0	7.6	15			1885	1.00	1620	1.00	5000	1. 0
1	7.5	19	76.6	15.1 (at 30 min.)	1882	1.00	1510	0.93		
2	7.3	22		26.6	1590	0.84				
3	7.0	25			1338	0.71	1230	0.76	3500	0.70
4	6.5	27		41.8	1300	0.69				
5	5.5	28	75.6		1218	0.65	1050	0.65		
6	5.2	29			1088	0.58				
7	4.9	30		50.0	1015	0.54	870	0.54	2050	0.41

TABLE 22. BATCH RUN DATA SHEET

Run #7A (No UV radiation)

Date: 7/10/78

Voltage: 450V

Gas Flow Rate: 4.5 CFM

No. of UV Lamps Used: 0

Mixer Speed R.P.M.: 314

Time Hr.	pH	Temp. °C	O_3 Concentration Mg/liter		Total Carbon Mg/liter	TC Fraction Remaining	TOC Mg/l	TOC Fraction Remaining	COD Mg/l	COD Fraction Remaining
			Inlet	Outlet						
0	7.9	30			547	1.00				
1	7.2	32	57.4	26.8	440	0.80				
2	7.1	34			358	0.65				
3	7.2	35		32.2	286	0.52				
4	7.2	30			233	0.43				
5			62.6	50.1						
6	7.6	31			133	0.24				
7										
8	7.8	33			82	0.15				
9			62.3	48.0						
10	8.6	34			80	0.15				

TABLE 23. BATCH RUN DATA SHEET

Run #7B (4 UV Lamps)

Date: 7/10/78

Voltage: 450V

Gas Flow Rate: 4.5 CFM

No. of UV Lamps Used: 4

Mixer Speed R.P.M.: 314

Time Hr.	pH	Temp. °C	O_3 Concentration Mg/liter		Total Carbon Mg/liter	TC Fraction Remaining	TOC Mg/l	TOC Fraction Remaining	COD Mg/l	COD Fraction Remaining
			Inlet	Outlet						
0	7.9	30			621	1.00				
1	7.1	33	57.4	23.1	457	0.75				
2	7.1	34			392	0.63				
3	7.2	36		30.6	333	0.54				
4	7.2	33			227	0.37				
5			62.6	42.6						
6	-	33			81	0.13				
7										
8	8.0	36	62.3		85	0.14				
9				40.4						
10	8.5	34			73	0.12				

TABLE 24. BATCH RUN DATA SHEET

Run #8A

Date: 7/12/78

Voltage: 450V

Gas Flow Rate: 4.5 CFM

No. of UV Lamps Used: None

Mixer Speed R.P.M.: 314

Time Hr.	pH	Temp. °C	O_3 Concentration Mg/liter		Total Carbon Mg/liter	TC Fraction Remaining	TOC Mg/l	TOC Fraction Remaining	COD Mg/l	COD Fraction Remaining
			Inlet	Outlet						
0	7.1	24			735	1.00				
1										
2	7.0	31	61.7		497	0.68				
3										
4	6.8	33		36.0	347	0.47				
5										
6	6.9	30		48.9	251	0.34				
7			62.1							
8	7.1	31			196	0.27				
9										
10	7.4	33		52.0	149	0.20				

TABLE 25. BATCH RUN DATA SHEET

Run #8B

Date: 7/12/78

Voltage: 450V

Gas Flow Rate: 4.5 CFM

No. of UV Lamps Used: 4

Mixer Speed R.P.M.: 314

Time Hr.	pH	Temp. °C	O_3 Concentration Mg/liter		Total Carbon Mg/liter	TC Fraction Remaining	TOC Mg/l	TOC Fraction Remaining	COD Mg/l	COD Fraction Remaining
			Inlet	Outlet						
0	7.1	24			680	1.00				
1										
2	7.0	31	61.7		467	0.69				
3										
4	6.9	34		35.5	302	0.44				
5										
6	7.0	30		45.9	228	0.34				
7			62.1							
8	7.3	32			166	0.24				
9										
10	7.5	33		51.7	136	0.20				

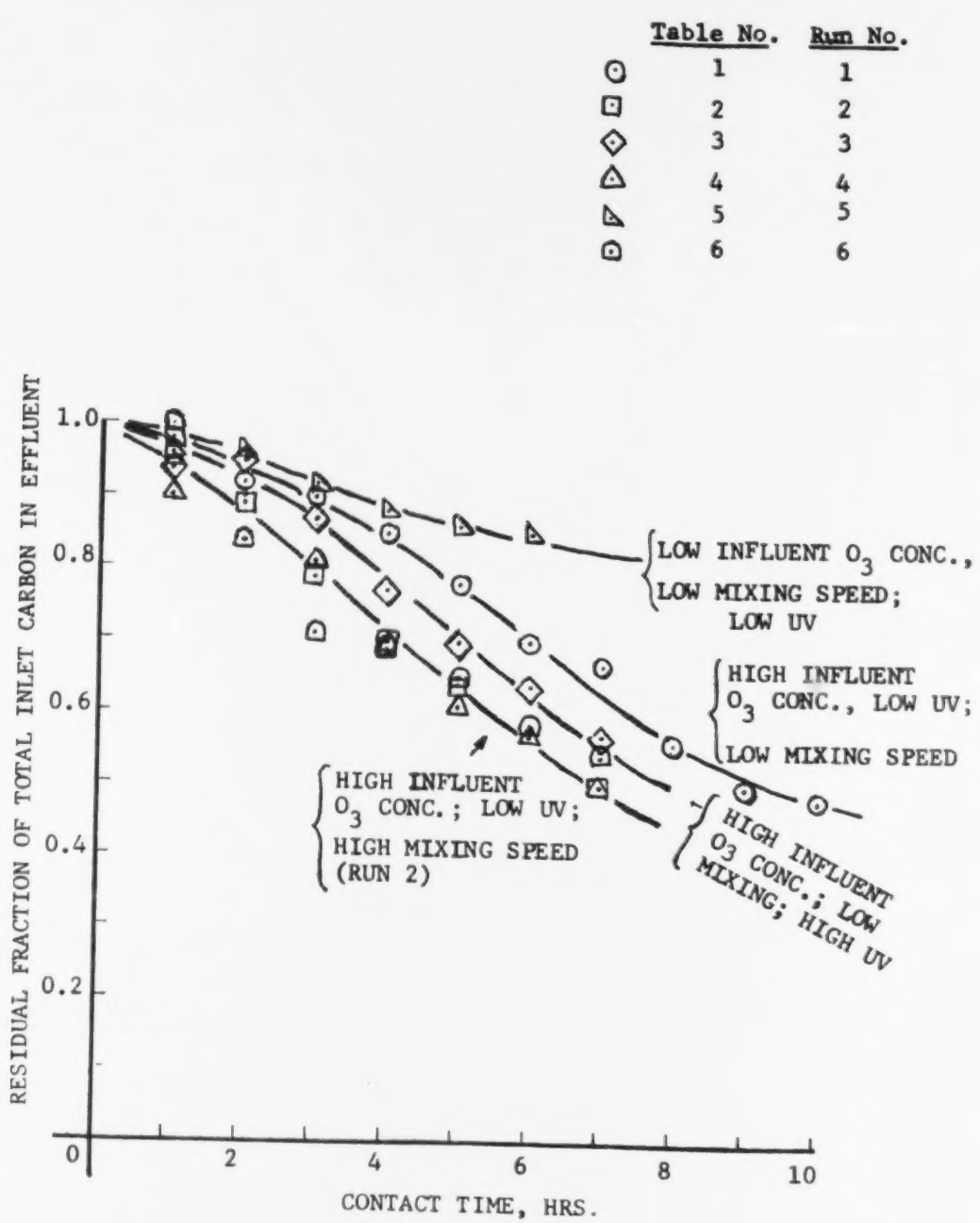


Figure 17. Effect of various process parameters on organics removal; batch test data.

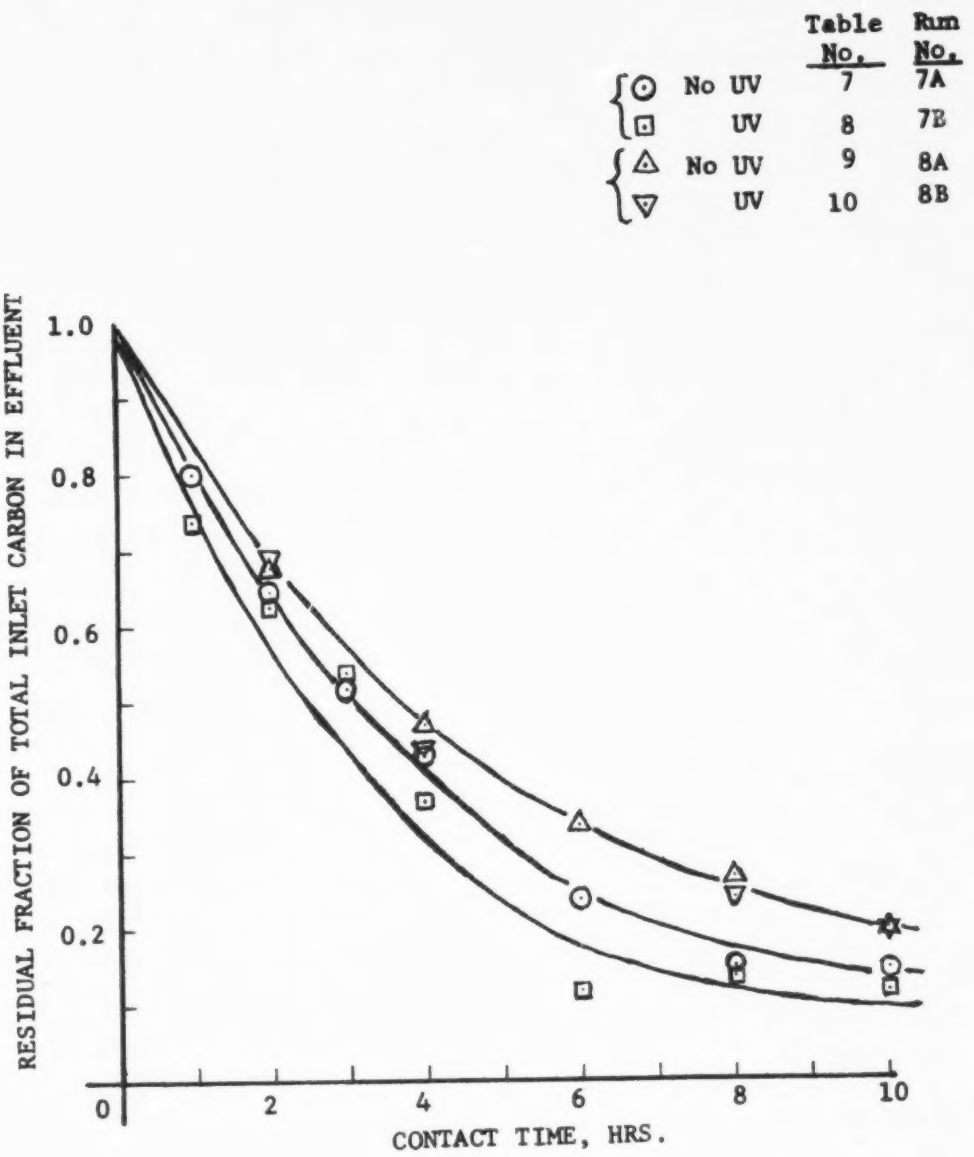


Figure 18. Effect of UV on organics removal; batch test data.

composition of the waste. An overall higher rate of reduction of organics in runs 7 and 8 (Figure 18) as compared to runs shown in Figure 17 is attributed primarily to their lower starting concentration which illustrates the importance of the influent organics concentration.

Based on the above results and analysis, detention time, influent ozone concentration, mixing speed, and influent organics concentration are considered to be the primary process variables. Other variables of interest are UV intensity and gas flowrate.

Flow Tests Data

The two reactors were connected in series for these tests and data were obtained under a variety of test conditions summarized in Table 26. Based on the results of the batch tests, mixing speed and the influent ozone concentration in all flow tests were kept at a maximum to achieve conditions favorable to rapid oxidation of dissolved organics. Conditions were varied with respect to liquid flowrate, gas flowrate, and UV intensity. Effects of pH and reaction temperature were also investigated. Data and measurements from these tests are given in Table 27. These include liquid flowrates, ozone concentrations in the influent to and the effluent gases from each reactor, reaction temperature, and pH, total carbon concentration, COD, and BOD of liquid streams for each reactor and the carbon column.

It may be mentioned that the maximum ozone concentration in a gas stream from an ozonator is a function of the gas flow-rate through it. Within the range investigated in this study, as the gas flowrate increased, the maximum ozone concentration decreased. This is reflected in the influent ozone concentration data in Table 27.

Data on organics concentration measured as total carbon for the influent to reactor 1, and the effluent of the two reactors for each run are shown in Figure 19. Experimental conditions for each run are also indicated along the horizontal axis. As seen in Figure 19, there was a considerable day-to-day variation in the influent waste concentration during the experimental period; the lowest value was ~500 mg/ℓ of total carbon while the highest was ~2160 mg/ℓ of total carbon concentration. Corresponding CODs are estimated at 1200 and 6000 mg/ℓ, respectively. Over the entire experimental period, the influent concentration average is calculated to be ~1400 mg/ℓ of total carbon (~3700 mg/ℓ COD), which is 2-3 times higher than the concentrations measured in similarly pretreated and sand-filtered effluent at the Swedesboro, N.J. terminal during an earlier small scale field test program. Obviously, the influent concentration is an important parameter since the overall system and treatment cost to a large degree is going to be proportional to the concentration of the waste influent and the degree of removal required.

Another result which is obvious from Figure 19 is that for the influent waste, flowrate of 2 ℓ/min or so is too high to achieve a high percent reduction in organics concentration. Effluent concentrations of reactors 1 and 2 drop dramatically as the liquid flowrate is lowered to ~1 ℓ/min.

The process design parameters of most interest include organics removal efficiency as a function of detention time and ozone requirements to achieve a certain process performance. Calculations on percent reduction of organics achieved in reactors 1 and 2 under different experimental conditions and corresponding ozone utilization ratio which is defined as mg of ozone/mg of TC removed, were made from data in Table 27. These calculations were made in two different ways and in each case the approach was based on minimizing the effect of nonequilibrium conditions brought about by day-to-day variations in the influent organics concentration on the calculated process design parameter values. In the first case, the flow tests data shown in Figure 19 was categorized based on liquid flowrate and the influent pH, and for each category, areas under the three curves shown in Figure 19 were calculated to determine organics removal efficiency. An assumption underlying the above approach is that effects of variations in the rest of the variables, i.e., other than the liquid flowrate and the influent pH, are overwhelmed by day-to-day variations in the influent organics concentration. Calculated process design parameter values based on this approach are shown in Table 28.

The second approach is based on utilizing data from those periods during which influent to reactor 1 does not change appreciably, and yet each period is long enough for reactor 1 to approach steady state operating conditions. Such periods are 5/10-5/11, 5/17-5/18, 5/31-6/2 and 6/26/-6/29. For each of these periods, reactor 1 is assumed to approach equilibrium conditions near the end of the period assuming all other experimental conditions remained unchanged. A similar approach is adopted for calculating process design parameters for reactor 2. Calculated values based on this approach are shown in Table 29.

Overall there is seen to exist a good agreement in values reported in Tables 29 & 30 with the exception of the percent organics reduction value at 2.1 ℓ/min flowrate. Since the values in Table 29 are based on the overall data, it is suggested that they represent better accuracy. The data also show that an increase in pH tends to deteriorate the process effectiveness. Effects of other variables such as gas flowrate, UV intensity, and reaction temperature could not be examined in detail since their effects were overwhelmed by the varying influent conditions.

The behavior of ozone concentration in effluent gases with respect to liquid flowrate and influent waste concentration as shown by the data in Table 27 is as expected; as liquid flowrate or influent organics concentration increases, the effluent ozone concentration in gases decreases.

TABLE 26. FLOW EXPERIMENTS CONDITIONS

Total reaction vessel volume	= 467 liters
Liquid flowrate	= 1.0 - 2.1 liters/min
Mixing speed	= 314 RPM
Gas flowrate in each reaction vessel	= 3 - 6 SCFM
Concentration of ozone in influent gas	= 54 - 74 mg/liter
UV intensity in each vessel (Lamp Wattage)	= 130 - 260 W
Reaction temperature	= 26 - 40^{o} C
Influent pH	= 5.5 - 10.0
Influent TC	= 500 - 2179 mg/liter
Influent COD	= UP to 6360 mg/liter
Carbon column volume	= ~10 liters
Flowrate through carbon bed	= 40 - 50 ml/min
Carbon column retention time	= 250 - 200 minutes
Sodium nitrate concentration in ozonated effluent	= 1000 mg/l

TABLE 12: FLOW EXPERIMENTS - DATA SUMMARY TABLE

Run No.	Date	Liquid Flow-rate	Gas Flow-rate	UV Lamps	O_3 In	O_3 Out		Reaction Temp.		Influent				Effluent I				Effluent II				Column Influent				Column Effluent			
				On		I	II	I	II	pH	TC	COD	BOD	pH	TC	COD	BOD	pH	TC	COD	BOD	pH	TC	COD	BOD	pH	TC	COD	BOD
		l/m	CFM		Mg/l	Mg/l		°C	°C																				
1	5/8	1	3	2	74						945 1032	2820																	
2	5/9	1.2	3	2	73	6	22	26	27	6.7	1018	2493		6.7	840-662	1640		6.1-5.7	752-600	1400						6.0	55	60	
3	5/10	0.95	3	2	73	15-24	29-35	27	30	6.7	768	1800		6.5-6.1	548-295	887		5.6	508-182	853-780						6.6	402	920	
4	5/11	1	3	2	73	20	34-44	26	29	6.7	824	2070		6.3	231-179	342		6.5	131-74	220						6.6	359	810	
5	5/12	1.1	3	2	73	26-13	40	26	30	6.8	1055			6.0	244 301			6.4	110-103							6.5	212		
6	5/15	2.0	3	2	72	8	17	21	24	7.0	1345			6.8-7.2	555-943			6.3-6.7	221-448							6.7	184		
7	5/16	2.1	3	2	73	7	14	21	24	7.1-6.8	1567			7.2	1120			6.9	606-691							6.8	298		
8	5/17	2.1	3	2	76	6	12	22	24-29	6.5	2179	5240		5.7	1019-1603			6.6	638-999	1800-2280						7.0	367		
9	5/18	2.1	3	2	71	6	9	25	28	6.5	2159	6360	3310	6.5	1553-1753			6.5	1003-1384	3680-4120	2750-3950					6.9	497		650
10	5/19	2.0	3	2	73	8	12	25	31	6.9	1729			6.9	1695-1443			6.8	1572-1366							5.9	1001		
11	5/22	2.0	3	2	72	7	14	31	36	7.0	1502			7.2	1282-1119			7.2	1200-1017							5.7	1086		
12	5/23	2	3	2	67	7	8	36	41	7.0	1136			7.2	1014-679			7.3	1011-752							5.8	882		
13	5/24	2	4.5	2	65	8	18	35	40	6.8	762			7.0	494-323			7.2	434-142							6.0	661		
14	5/25	2	4.5	2	67	12	44	35	38	6.7	500			7.0	281-95			7.2-7.8	105-56							6.3	425		
15	5/26	2	4.5	2	67	16	46	35	37	6.7	558			6.9-6.5	98-136			7.7-7.4	61	24	8					5.8	11		
16	5/30	1	4.5	5	60	15	38	28	30	6.6	1452			6.8-5.7	267-485			7.0-6.6	83				69				10		
17	5/31	1.1	4.5	4	64	13	26	33	36	6.7	1700	5300	1120	5.8	552-659	1520	760	6.0	118-168	160	50		91			6.4	50	29	<10
18	6/1	1.	4.5	4	63	9	21	33	40	6.7	1731			5.8-6.1	656-762			5.8-6.6	161			6.3	136			6.7	89		
19	6/2	1.1	4.5	4	63	6	15	30-	35-	6.6	1600	4980	1450	6.5	836-860	1952	930	6.6	228-195	208	110	6.6	164			6.6	115	73	19

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(continued)

TABLE 12: FLOW EXPERIMENTS - DATA SUMMARY TABLE (Continued)

Run No.	Date	Liquid Flow rate l/m	Gas Flow rate CFH	UV On	O_3 In mg/l	O_3 Out I mg/l	O_3 Out II mg/l	Reaction Temp. I °C	Reaction Temp. II °C	Influent pH	Influent TC	Influent COD	Influent BOD	Effluent I pH	Effluent I TC	Effluent I COD	Effluent I BOD	Effluent II pH	Effluent II TC	Effluent II COD	Effluent II BOD	Column Influent pH	Column Influent TC	Column Influent COD	Column Influent BOD	Column Effluent pH	Column Effluent TC	Column Effluent COD	Column Effluent BOD
20	6/7	1.0	6.0	4	56	8	32	29-34	28-35	5.7	1820	5160	2450	5.8	507-670	808	804	7.2	190	198	99	7.6	184			7.5	151	46	13
21	6/8	1.1	6.0	4	54	8	25	30	33	5.5	2007			5.5	700			6.4	185			7.5	201			7.7	179		
22	6/9	1.1	6.0	4	54	14-24	26	31	34	6.1	1608			4.9-4.2	615-562			5.4-4.7	184-210			7.4	204			7.6	172		
23	6/12	1.1	6.0	4	55	11-37	34	29	32	6.0	1154			4.2	575-500			4.4	179-302			4.6	223			7.2	148		
24	6/13	1.1	6.0	4	55	36	35	25	31	6.5	1038	3227		4.6-5.0	508-533	1448		4.5	293-328	816		4.6	276			7.1	104	102	
25	6/14	1.2	6.0	4	55	33	46	22	26	6.5	903			5.3-5.9	463-399			4.6-4.9	336			4.7	295			6.5	128		
26	6/15	1.1	4.5	4	65	25	49	26	30	6.6	1093			6.1	380			5.3	310			5.1	326			6.3	140		
27	6/16	1.2	4.5	4	61	20-36		27	32	6.7	1850			5.4	550-740			5.7-5.3	286-411			5.3	300			6.2	175		
28	6/19	1.1	4.5	4	58	15	32-48	31	33	9.3	1858			5.6	806			5.7	575-493			5.3	356			7.4	419		
29	6/20-6/22																					5.6	375			7.0	250		
30	6/23	1.3	4.5	4	62	26	30	28	31	9.2	1617	5046		5.8	835	2196		5.9	457-530			5.5	368			6.4	234 TOC-186	486	
31	6/26	1.1	4.5	4	61	28	40	30	32	9.7	1724			5.8	914			5.5	520-603			5.7	464			6.4	358		
32	6/27	1.1	4.5	4	61	17	38	31	36	9.9	1709-1665	5665		6.0	949			5.0	636			5.7	480			6.4	359-308	792	
33	6/28	1.1	4.5	4	56	15	29	34	39	10.0	1776			7.1	954-850			6.3	620-673			5.7	616			6.4	432-360		
34	6/29	1.2	4.5	4	58	14	32	35	37	9.9	1561 1596			7.3	870			7.1	576			6.4	621			6.4	507		
35	6/30	1.1	4.5	4	62	20	32	34	37	9.9	1317			7.6	817-645			7.4	503			6.5	595			7.1	532		
36	7/5	1.2	4.5	4	63	23	36	25	26	9.9	1010	2666	1020	7.8	639-576	1228	550	7.6	411		370	7.2	492			7.1	499	1089	619
37	7/6	4.5	4.5	4	62	27	38	30	32	10.1	852			7.9	532-372			7.9	412-278			7.7	424			7.4	439		

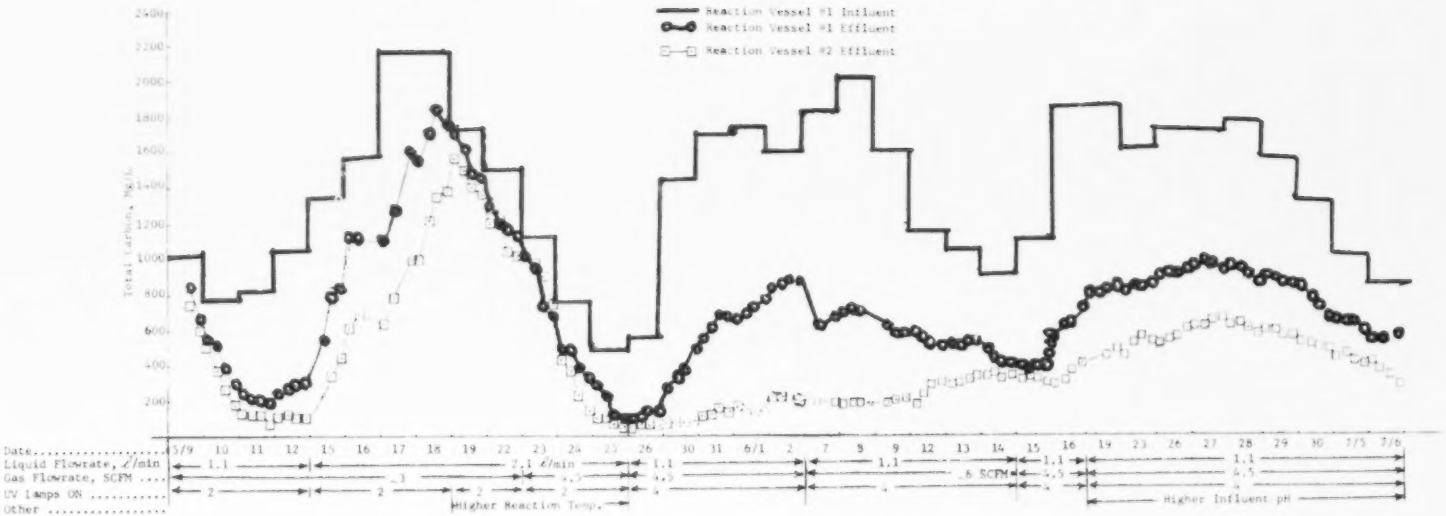

Figure 7. Total carbon measurements for flow tests.

TABLE 28. OZONATOR CAPACITY AND CAPITAL COST ESTIMATION

	Case 1	Case 2
Flow Rate	15000 GPD	15000 GPD
Influent TC	800 mg/l	1500 mg/l
COD	2030 mg/l	4000 mg/l
Assume final effluent TC	225 mg/l	225 mg/l
COD	400 mg/l	400 mg/l
% removal (TC basis)	71.8%	85%
(COD basis)	80%	90%
Required COD removal capacity	202 lb	446 lb
Mg O_3/mg TC removed	8	8
Ozone required	570 lb	1263 lb
	600 lb	1330 lb assuming 95% utilization efficiency
		1350 lb capacity
Ozonator capital cost*	$200K(1)	$300K(2)
Reactor vessels 20% of ozonator cost	$ 40K	$ 60K
Total capital cost	$240K	$360K

* Based on an estimate of $250,000 for a 1000 lb/day ozonator obtained from Emery Industries, Inc.

(1) Assumed 80% of the cost of a 1000 lb ozonator.

(2) Assumed 120% of the cost of a 1000 lb ozonator.

TABLE 29. ORGANICS REMOVAL AND OZONE UTILIZATION EFFICIENCIES: CUMULATIVE DATA BASE

Experimental Conditions	Data Base Period	Calculated % TC Reduction		Calculated Avg. TC Conc., mg/l			Calculated Ratio $\frac{mg\ O_3\ used}{mg\ TC\ removed}$	
		Reactor 1	Reactors 1 & 2	Inf.	Eff.1	Eff.2	Reactor 1	Reactors 2
1. Liquid @ 1.1 l/min; pH unadjusted; gas @ 4.5-6 SCFM	5/30-6/16	61	84	1400	540	215	6.1	11.2
2. Liquid @ 1.1 l/min; high pH; gas @ 4.5 SCFM	6/19-7/6	46	65	1450	780	505	6.8	10.6
3. Liquid @ 2.1 l/min. pH unadjusted; gas @ 3-4.5 SCFM	5/15-5/26	31	47	1400	975	735	6.6	9.4
4. Liquid @ 1.1 l/min. gas @ 3-6 SCFM (includes 1 and 2)	5/9-5/12 5/30-6/16 6/19-7/6	55	76	1347	600	320	6.5	11.8

COMPOSITE OZONE UTILIZATION RATIO CALCULATION

DATA BASE:	5/30-6/16	All data at 1.1 l/min: 5/9 -5/12 5/30-6/16 6/19-7/6
% of Total Reduction in Reactor 1	72.7%	72.4%
% of Total Reduction in Reactor 2	27.3%	27.6%
Composite Ozone Utilization Ratio	7.5	8.0

TABLE 30. ORGANICS REMOVAL AND OZONE UTILIZATION EFFICIENCIES FOR SELECTED PERIODS

Period	Experimental Conditions	Steady-State TC Concentrations			% TC Reduction		Calculated Ratio, mg Ozone Used / mg TC Removed	
		Influent 1	Effluent 1	Effluent 2	Reactor 1	Reactors 1 & 2	Reactor 1	Reactor 2
5/10-5/11	Liquid @ 1.1 l/min; pH unadjusted; gas @ 3 CFM	796	198	104	75	88	6.0	27.5
5/17-5/18	Liquid @ 2.1 l/min; pH unadjusted; gas @ 3 CFM	2169	1836	1572	15	27	8.0	10.0
5/31-6/2	Liquid @ 1.1 l/min; pH unadjusted; gas @ 4.5 CFM	1643	856	210	48	87	8.3	8.5
6/7-6/9	Liquid @ 1.1 l/min; pH unadjusted; gas @ 6 CFM	1811	580	198	68	89	4.4	11.1
6/26-6/29	Liquid @ 1.1 l/min; high pH; gas @ 4.5 CFM	1692	867	576	49	66	6.6	11.8

Reaction temperature in each vessel was observed to increase as a run progressed during the day. The increase depending on ambient conditions was usually 3-8°C in each vessel, usually more in the second than the first one. The temperature increase must be due to the energy dissipation of the UV lamps in water. An increase in temperature decreases ozone solubility in water while increasing the reaction rate. The data does not permit a quantitive estimation of this effect. However, it is believed that the net effect may be small compared to the effect of varying influent conditions.

Carbon Column Data

Column performance data are summarized in Figure 20 for the test period 5/31-6/30. Both the influent and effluent organics concentrations are shown in terms of total carbon. Fresh carbon was charged into the column on 5/26 and was seeded with biological microorganisms using industrial effluent from the Rollins Environmental Services waste treatment plant at Logan, New Jersey. The seeding effluent was continuously circulated through the column for three days. The column was fed ozonated effluent starting 5/30. Based on data shown in Figure 20, ~36% organics removal was achieved in the carbon column during the first four weeks, 5/31-6/25. During the following week, the column performance deteriorated. A sulfide odor was detected in the column effluent which indicated the existence of biological activity although under anaerobic conditions in the column. To counter anaerobic conditions in the column which were considered responsible for deterioration in its performance, a 1000 mg/ℓ of sodium nitrate addition to the column influent was started. Within 2-3 days, the sulfide odor in the effluent had disappeared. A microscopic examination of the column effluent showed the presence of microorganisms which further confirmed the existence of bio-organisms in the column. This result is quite significant for potential application of a carbon column as a biological reactor for polishing ozonated effluent.

Correlation of Total Carbon with COD and BOD

The COD and BOD data reported in Tables 16 to 25 and 27 for batch and flow tests are used to develop correlations with total carbon concentrations. These correlations are shown in Figures 21 and 22 respectively. Notice that the COD correlation can be satisfactorily applied over a much wider range than the BOD correlation. It is recommended that BOD correlation be applied on lower concentration levels only and should not be extrapolated without extending the actual data base.

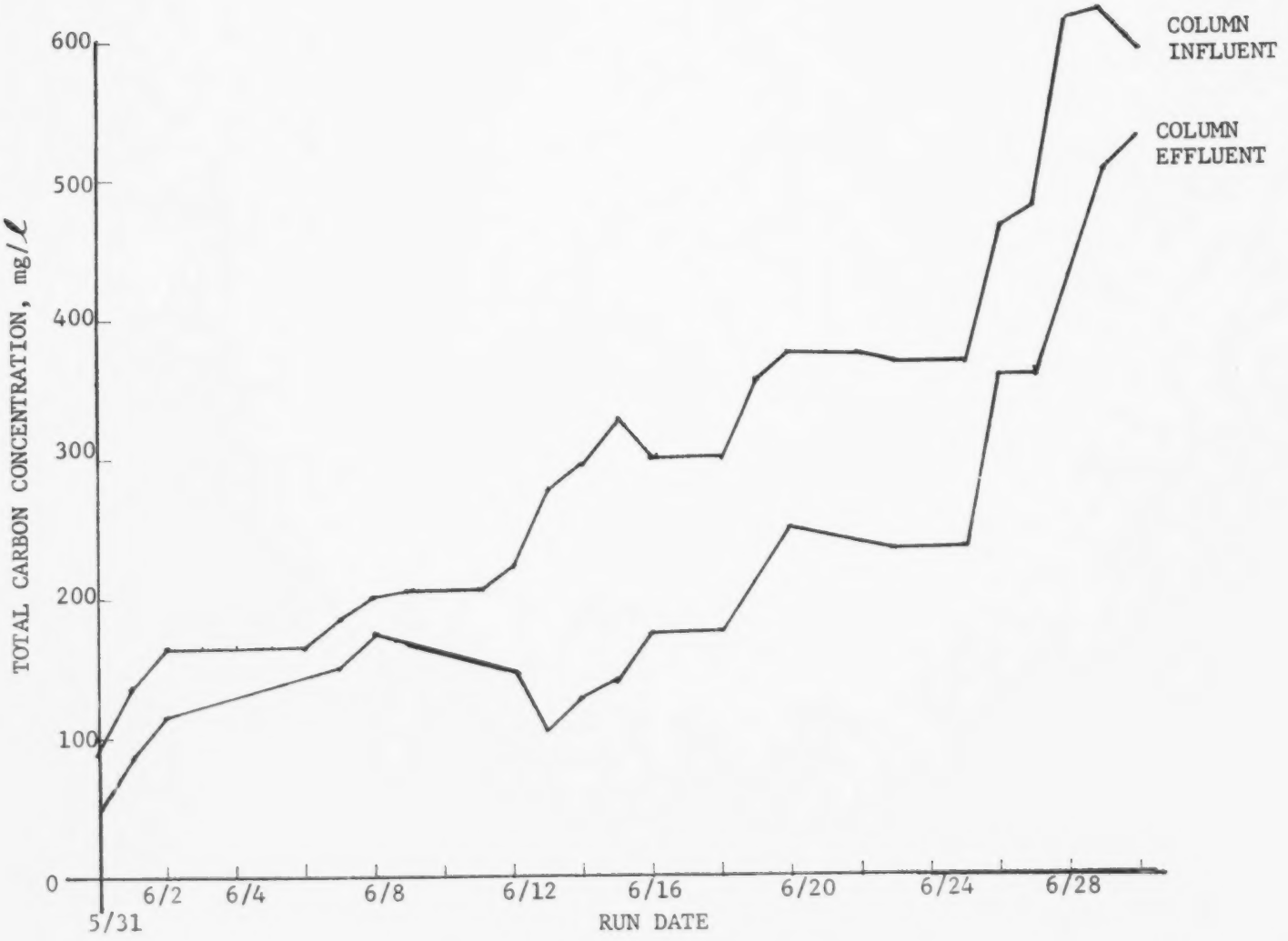

Figure 20. Carbon column data summary.

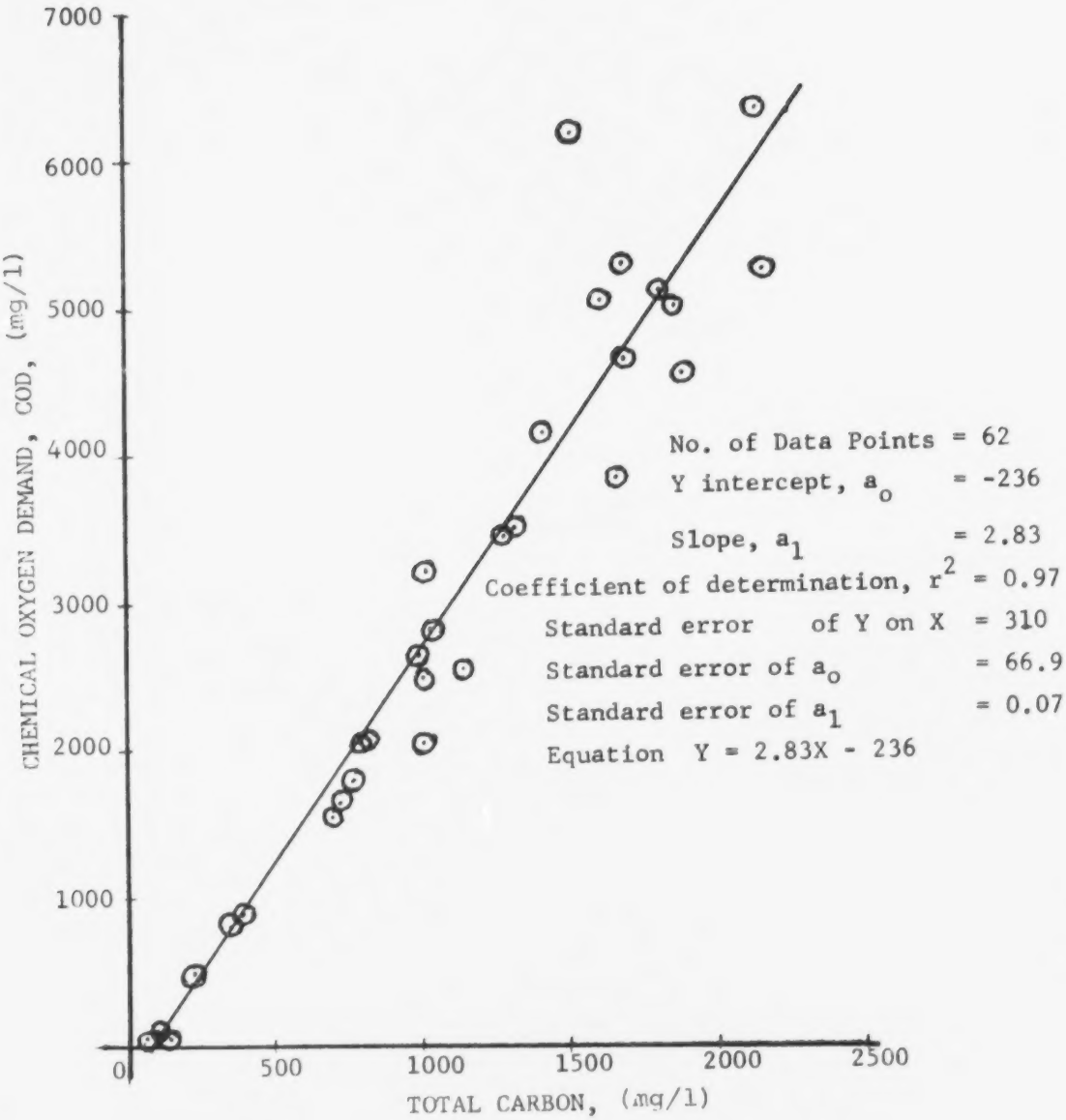

Figure 21. Total carbon vs. COD correlation (Batch and flow tests data).

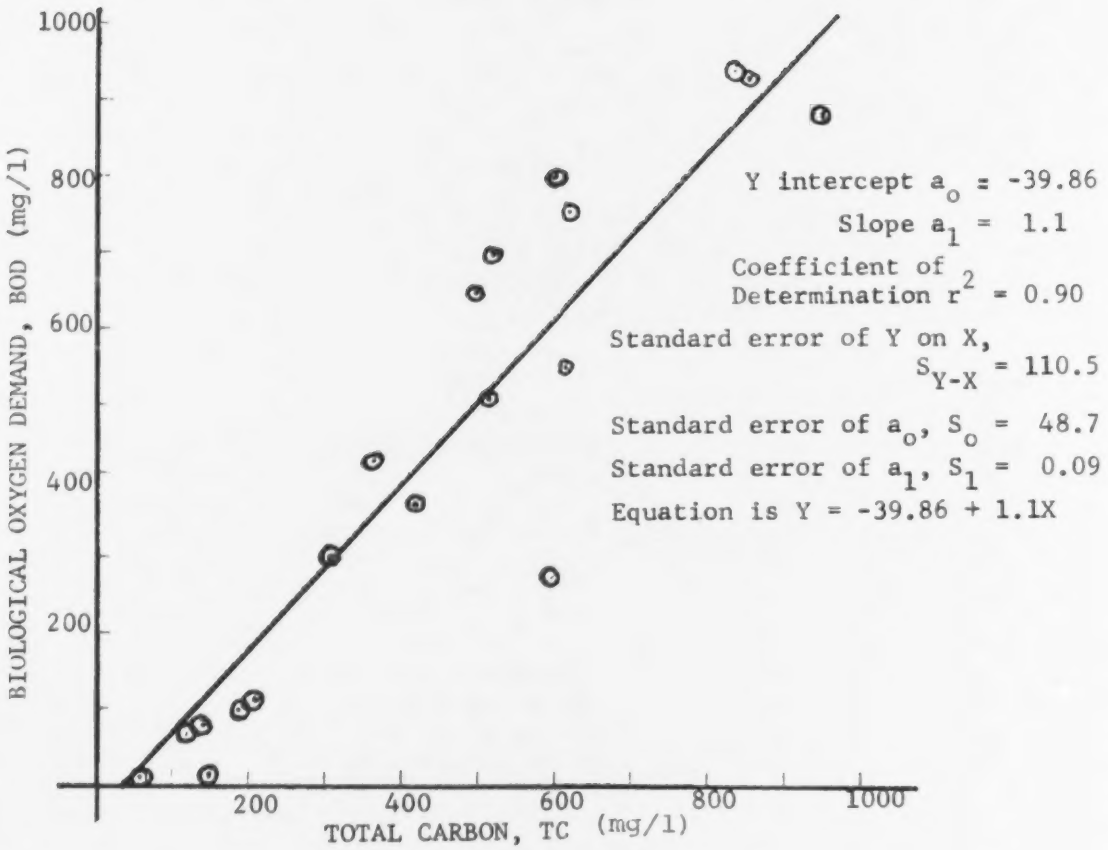

Figure 22. Total carbon vs. BOD correlation (Batch and flow tests data).

Experimental Observations

Foaming was observed to occur as influent waste was contacted with gases. It occurred to a significantly larger extent in reaction vessel 1 than in 2, and at a higher gas flowrate. During the period of 6/12-6/15, foaming caused gas flowrates in the two reaction vessels to go out of balance. Most of the gas was going into one reactor instead of being equally divided between the two. That is the reason for little additional reduction in organics concentration in reaction vessel 2 during 6/14 and 6/15. Apparently due to heavy foaming in reactor 1, a substantial portion of the liquid was displaced into the second reactor which resulted in different head pressures in the two vessels, and hence the unbalanced gas flowrates. Also, foam occasionally blocked the gas exhaust line from the first reactor which again led to imbalance of gas flowrates into the two reactors. Such a condition should be detected from the manometers attached to each reaction vessel and was corrected by draining the exhaust line. In the latter portion of the experimental period, foaming was controlled by periodic addition of a small amount, 10-20 cc, of a defoaming agent (GE Antifoam 60, Silicone Products Division). Contributions of this agent to organics concentration in waste were analyzed to be insignificant.

DISCUSSION

Based on the results and the analysis presented above, primary process parameters are liquid retention time (or flow rate) which is directly affected by the influent waste concentration, influent ozone concentration, and mixing speed. Other variables that may affect are gas flowrate, UV intensity, pH, and reaction temperature; however, within the experimental range investigated in this study, their effects were not observed to be significant. The main reason for this is considered to be the highly and rapidly varying influent conditions which overwhelm any changes due to the above-mentioned parameters. Due to continuous and irregular day-to-day variations in the influent waste concentration, steady state in either of the reactors is seldom achieved as is evident from Figure 19. For a constant, stirred tank reactor vessel of 467 liters capacity and an average liquid flowrate of 1.15 ℓ/min, it can be calculated that approximately 14 hours will be required before 92% of the liquid is replaced, assuming 20% of the vessel capacity is taken up by gas. This means that the influent concentration must stay unchanged for at least 2 days(@ 7-8 hours /run) for reactor 1 effluent to approach steady-state conditions. By similar reasoning, effluent of reactor 1 which is influent of reactor 2 must stay constant for at least two days before effluent of reactor 2 will approach equilibrium. An examination of Figure 19, quickly shows that this condition was only infrequently achieved.

Based on calculations of process effectiveness as defined by percent reduction in total carbon in Table 29 or 30, it is clear that the process can achieve removal efficiency of 75-85%. In terms of COD or BOD removal, efficiency may well exceed 90% since the ratio of COD or BOD to total carbon decreases as concentration drops.

From Table 28 or 29, it is seen that ozone utilization ratios for the first reactor are always lower than those for the second. One reason may be that the influent waste is a mixture of different chemicals, some of which are more readily oxidized than others. Another reason may be that products of reaction from the first-stage of ozonation are more resistant to further oxidation by ozone. A more likely situation is that both conditions exist.

According to a simplified reaction scheme, each molecule of ozone dissociates into one oxygen molecule and a singlet oxygen atom, O; the latter then reacts with organic carbon to form CO_2. Thus, two ozone molecules will be required to oxidize one atom of carbon. The theoretical ratio of mg of ozone used per mg of carbon removed according to such a reaction scheme is 8. That it is generally less than 8 for the first reactor as shown in Table 29 or 30 may, in part, be due to the fact that the waste includes a certain small fraction which is oxidized by oxygen. This, for all practical purposes, would be limited to the first reactor only since the bulk of the waste is resistant to oxidation by oxygen.

FULL SCALE PROCESS DESIGN

From the process design viewpoint, it is desirable to achieve the highest treatment efficiency while maintaining the lowest ozone utilization ratio. The two requirements are in conflict since to achieve a high removal efficiency, a constant, stirred tank reactor must be operated at a low concentration; while to achieve a low ozone utilization ratio, a high waste organics concentration in the reactor is desirable. A design concept based on multiple reactors and recycling, however, can help to a great extent in meeting both objectives at the same time.

For a full scale process design, the two critical parameters are ozone requirement and gas-liquid contact time. The ozone requirement is a direct function of the influent waste concentration. The higher the influent waste concentration, the higher the ozone requirement, assuming effluent criteria remain unchanged. As stated earlier, the influent was 2-3 times more concentrated in dissolved organics during the current test program than in an earlier field test which was conducted at a different location. Basic operations of truck cleaning which generated the wastewater and pretreatment schemes for the removal of floating and suspended matter were identical at both locations. For process design and cost estimation purposes, two cases are selected; one, influent waste at 800 mg/ℓ of total carbon concentration (~2030 mg/ℓ of COD), and second, influent waste at 1500 mg/ℓ of total carbon concentration (~4000 mg/ℓ of COD). Process capacity is selected at 15000 gpd which is typical of Matlack terminals. It is further assumed that the ozonated

effluent will have a residual total carbon concentration of 225 mg/ℓ (~400 mg/ℓ of COD). This value is purposely selected at a high enough level in order to maintain an acceptable ozone/organic carbon ratio. A drop in the concentration level will result in increasing the ratio and hence requiring more ozonator capacity. The data in Table 30 show that at a concentration level of ~100 mg/ℓ of total carbon, the ratio more than doubles which means capital and operating costs will start increasing at a very rapid rate if concentrations in the last reactor were lowered much below the 225 mg/ℓ organic carbon level. These design conditions are listed in Table 28. For sizing the ozonator, ozone utilization ratio of 8 is used based on calculation of the composite ozone utilization ratio in Table 28. For the two cases being considered, ozone requirements are estimated at 600 and 1350 lb/day, respectively. Capital cost for an ozonator for each case is estimated based on an estimate obtained from Emery Industries, Inc., for a 1000 lb. ozonator.

For gas-liquid contacting, a multiple reactor scheme is proposed, based on scale-up of the pilot scale reactors. Two reactors will be needed in either case. For the more concentrated influent, a third stage may be needed. Additional cost for the third stage has already been included in the capital cost estimate by costing the reactor vessels as a fixed percentage of the ozonator cost. Each contactor is sized to provide 8 hours of contact time. The capacity of such a vessel is calculated to be ~5700 gallons, approximately 7 ft diameter and 20 ft high. Vessel sizing includes a freeboard volume of 8%. Costing for the reactor vessel is estimated based on weight of steel involved in a tank, and includes allowance for accessories such as mixing device, UV lights, fittings, and instrumentation.

Provision for recycling in the full scale prototype system is also recommended. Although its effect was not investigated in this study, recycling in each reactor is expected to increase efficiency of ozone utilization. A 50-75% of recycling of effluent stream is recommended for prototype system design purposes.

Estimated operating costs for the two cases being considered are shown in Table 31. Overall daily oxygen consumption is estimated at ~150% of the COD removed to take into account the loss of oxygen during bleed-off from the gas stream. It is assumed that no additional labor will be required for the ozonation system. Operating costs for the two cases were estimated at 1.36 and 2.42 cents/gallon. Almost 50% of this cost is due to the depreciation of the ozonator which is depreciated over a period of 8-1/2 years at 4% annually. The 8-1/2 years lifetime is considered to be unrealistically short since according to several ozone generator manufacturers, a generator may last for 40 years and more. Using a 25-year period for depreciation of the ozonator which is more realistic, yet conservative, the operating costs for the two cases are calculated at 0.97 and 1.74 cents/gallon which are substantially lower than the estimates in Table 31.

TABLE 31. ESTIMATE OF OPERATING COSTS FOR A FULL-SCALE OZONATION PROCESS ¢/GALLON

	CASE 1 ¢/gallon	CASE 2 ¢/gallon
Oxygen	0.07 (1)	0.15 (2)
Power for Ozonator	0.60 (3)	1.23 (4)
Depreciation	0.62 (5)	0.93 (5)
Maintenance	0.07 (6)	0.11 (6)
Labor	- (7)	- (7)
TOTAL	1.36	2.42

(1) 300 lb/day @ $70/ton for oxygen consumption.

(2) 650 lb/day @ $70/ton for oxygen consumption.

(3) 150 KW @ 2.5¢/KW Hr (6 KWHr/lb ozone).

(4) 310 KW @ 2.5¢/KW Hr (5.5 KWHr/lb ozone).

(5) Depreciation over 8-1/2 years at 4% annually.

(6) @ 2% of capital cost annually for ozone generation equipment.

(7) Assumed that no additional labor will be required for the addition of an ozonation system.

To ensure an efficient contacting of gas and liquid, some sort of mixing will be required. The motor-driven turbine propeller type mixer such as the one used in this study does not seem to be practical for a full-scale process. Other devices commercially available need to be investigated. An example of such a device is a Frings immersible aerator which is self-aspirating. High gas transfer rates and efficiency are reported by the manufacturer for the device.

Based on the data obtained in this test, the effect of UV on the process effectiveness cannot be fully evaluated primarily due to large and rapid variation in the influent conditions. Preliminary indications based on batch data are that the UV may not be making a significant contribution to the overall process effectiveness. However, there are several reports in the open literature that have demonstrated its role in improving the process performance primarily by increasing the reactivity of organics to ozone. So it is recommended that the role of UV should be checked more thoroughly in the first full-scale prototype system. UV lamps may be installed in the second reactor only. Rationale for this recommendation is that the waste contains a large fraction of organics which readily react with ozone without UV; these will be reacted in the first stage. The data from this study show that more ozone is consumed per unit mass of organics oxidized in the second stage than in the first stage and that is where UV's contribution may be assessed.

Polishing

The ozonated effluent in the above proposed design has a residual concentration of 225 mg/ℓ of total carbon (~400 mg/ℓ COD). A polishing step based on carbon adsorption alone does not appear to be economically attractive since the data indicate that 15-20 hours of contact time may be required to achieve a low effluent organics concentration, say COD of 50 mg/ℓ. Furthermore, the capacity of carbon for removing the residual organics is yet unknown. It is, however, not expected to be as high following ozonation as before since smaller and more polar molecules are probably produced in the ozonation process which are less adsorbable. However, the possibility of using a biological oxidation-based polishing step in which carbon is used both as a substrate to grow microorganisms and an adsorbent is very promising. During this program, the capability of the microorganisms to survive a variety of influent concentrations has been demonstrated. Reversal of anaerobic conditions in the carbon bed by the use of sodium nitrate which is both a nutrient and a source of oxygen in microbiological reactions has also been demonstrated. It is recommended a polishing step based on this concept should be investigated further at the pilot scale.

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TABLE 32. SI CONVERSION FACTORS

AREA			
1 ft^2	=	9.290 304 E-02	m^2
1 in^2	=	6.451 600 E-04	m^2
LENGTH			
1 ft	=	3.048 000 E-01	m
1 in	=	2.540 000 E-02	m
MASS			
1 lb (avoirdupois)	=	4.535 924 E-01	kg
PRESSURE			
1 psi	=	6.894 757 E+03	Pa
VOLUME			
1 ft^3	=	2.831 685 E-02	m^3
1 gal (U.S. liquid)	=	3.785 412 E-03	m^3
1 gpd	=	4.381 264 E-08	m^3/s
1 gpm	=	6.309 020 E-05	m^3/s